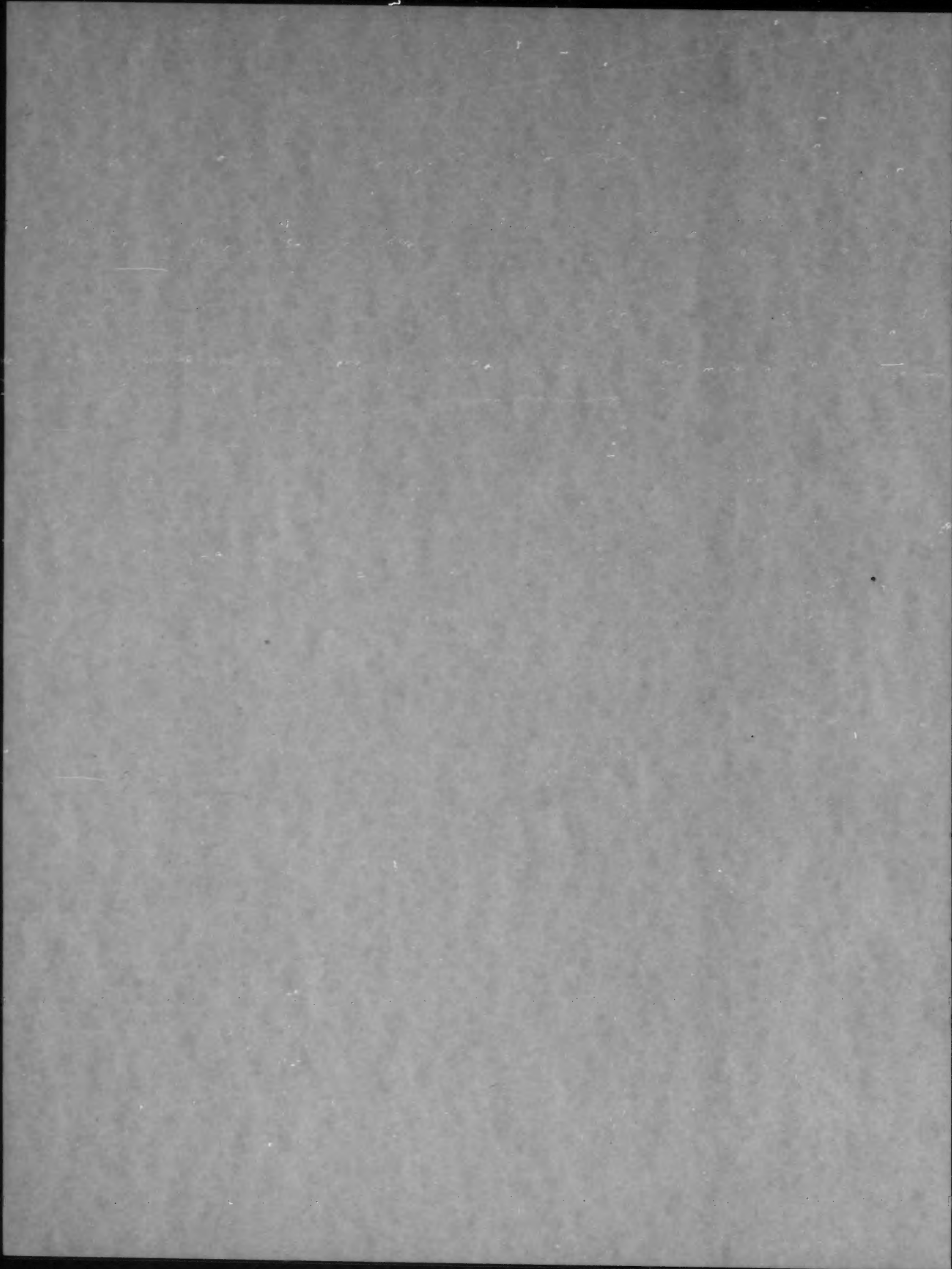


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POROUS STRUCTURE OF ADSORBENTS•

M. M. Dubinin

We have during the past few decades witnessed the ever increasing practical application of the phenomenon of adsorption. The most striking examples of technical adsorptional processes realized in the gaseous phase on an industrial scale are the recovery of volatile solvent vapors, the extraction of gasoline from natural gases, and the separation of mixtures of gases. Adsorbents are also widely applied to the purification of liquids and solutions. In all these cases we are concerned with porous adsorbents, which are also of separate interest to industry as carriers of catalysts.

The physical adsorption of gases, vapors, and solutes is basically dependent on the porous structure of adsorbents, which also determines their properties as catalyst carriers. The detailed study of adsorbent structure is hence not only of scientific, but also of considerable practical, interest.

Three kinds of pores are to be found in active charcoals, which are the most widely encountered adsorbents. The biggest are the macropores, which can in many cases be studied with the aid of the optical microscope (Fig. 1). The most suitable method for the detailed study of the distribution of the volumes of macropores according to their effective radii is that depending on the measurement of the volume of mercury, which does not wet the walls of the pores, filling the pores at different hydrostatic pressures. Each pressure P has a corresponding effective radius r , being that of the smallest of the pores filled at that pressure:

$$r = -\frac{2\sigma \cos \theta}{P}, \quad (1)$$

where σ is the surface tension of mercury, and θ is the angle of contact of mercury, which we find to be 142° .

A differential curve representing the distribution of pore volumes can be constructed from such measurements, and it is usually characterized by a maximum, corresponding with the prevailing pore diameter. Such maxima on the effective macropore radius distribution curves for various active charcoals fall within the limits 1000 - 10,000 Å. The largest macropores have diameters of the order of thousandths of a centimeter.

The macropores of active charcoals do not affect the values for sorption at equilibrium, and serve only as channels whereby the adsorbed molecules are enabled to penetrate into the interior of the grains of charcoal. The specific surface of the macropores does not exceed 1-2 sq. m. per g., so that the amount of substance adsorbed on their walls is negligibly small.

The transitional pores are smaller in diameter, and become filled with liquid as a result of the process of capillary condensation of vapors of organic liquids adsorbed therein. The non-coincidence of the sorptional and desorptional branches of the isotherms, to give a hysteric loop, is characteristic of capillary condensation. The volume of the transitional pores is equal to that of vapor (as liquid) sorbed between the equilibrium pressure at which hysteresis is first observed and the saturation value at the relative pressure $p/p_s = 1$ (Fig. 2).

According to the theory of capillary condensation, to each equilibrium vapor pressure there corresponds a definite radius of curvature of the meniscus, which is, under conditions of full wetting, equal to the radius of the free space between adsorption films in the smallest of the filled transitional pores. After introducing a correction for the thickness of the adsorption film we obtain the effective radius of the finest of the filled transitional pores. Such measurements, allowing for the amount of adsorbed vapor, enable us to construct differential curves representing distribution of volumes of transitional pores according to their radius.

The transitional porosity of active charcoals can in most cases also be studied by other methods, such as that of infiltrating mercury under pressure, or by means of the electron microscope (Fig. 3). The effective

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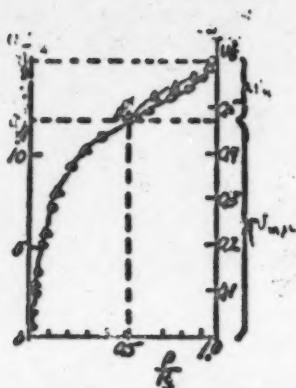


Fig. 2. Sorption and desorption isotherm for methanol vapor at 20°, on active charcoal.

radii of transitional pores of various active charcoals, corresponding with maxima on the distribution curves, fall within the limits 70-170 Å. Since the volumes of transitional pores of different charcoals vary within broad limits from the order of hundredths to tenths of a cc. per g., it follows that their specific surface may vary from a few square m. to 100 square m. per g.

The finest variety of pores are the micropores, which are too small to be seen even with the electron microscope. The study of adsorption from solutions of substances of different molecular sizes, i.e., the application of the method of "molecular sounds" developed by us, allows us to draw the conclusion that the dimensions of the micropores approach those of molecules. Such fine pores or free spaces in the crystalline structure formed by the not fully ordered spatial distribution of the six-membered elementary graphite rings in the turbostratic structure of carbon, give a very considerable specific surface due to micropores of active charcoal, of the order of hundreds of sq. m. per g.

Vapor adsorbed on the walls of micropores is transformed into liquid by the pressure exerted on it. The rapid increase in thickness of the adsorption layer, due to the considerably raised adsorption potential prevailing in the fine micropores, leads to their becoming filled with condensed vapor. The adsorption process is wholly reversible, i.e., the adsorptional and desorptional branches of the isotherms coincide.

In the case of limiting adsorption of sparingly soluble aliphatic acids and alcohols from aqueous solutions the micropores of active charcoal become filled with the pure solute, in the liquid state. The good agreement between the values for the volume of pores filled with condensed vapor at the point of beginning of hysteresis, or with acids or alcohols at limiting adsorption from solutions, served as a basis for the method developed by Kiselev for determination of the volume of the micropores of active charcoal. (For figures 1, 3, and 6, see Plate, page 557-a).

Thus the sorption of organic vapors by active charcoal is made up of an adsorption process leading to the filling up of the micropores, with usually unimportant values of multimolecular adsorption on the surfaces of the transitional pores, and of a process of capillary condensation, which leads to the filling up of the transitional pores. The only exception to this is that of sorption of water vapor, the molecules of which are considerably smaller than are those of organic vapors; the process of adsorption depends only on the relatively weak dispersive forces acting in the presence of the more powerful interaction of dipole water molecules with each other. All this leads to the filling up of the micropores basically as a result of capillary condensation of water vapor. The coarser transitional pores are not as a rule filled in the process of sorption.

As a result there arises the possibility of approximately calculating the distribution of micropore volume according to radii, based on the desorptional branches of the isotherms for water vapor. Such differential distribution curves exhibit a maximum, and give an approximate idea of micropore dimensions. The effective radii of micropores of various active charcoals, corresponding to the maxima of the distribution curves, fall within the limits 11-25 Å.

Fig. 4 presents a differential porosity curve for a specimen of charcoal prepared under such conditions as ensure development of all varieties of pores; the numerical data are taken from Aleksandrov, Zaverina, Plachenova, and Chepurmy. The first part of the curve, with a maximum at $r = 18$ Å corresponds to micropores with a volume of 0.19 cc per g and a specific surface of 240 sq. m. per g. It is derived from the desorptional branch for capillary condensation of water vapor. The second part of the curve, maximum at $r = 140$ Å, relates to transitional pores, volume 0.49 cc. per g., specific surface ~150 sq. m. per g. Curve 1, Fig. 4, is derived from the desorptional branch for capillary condensation of benzene vapor, without correcting for adsorbed vapor, and Curve 2 is derived from mercury infiltration experiments; the good agreement obtained by different methods for the differential distribution curves for transitional pores is worthy of note. Finally, the third part of the curve, with a maximum at $r = 7900$ Å, relates to the macropores, volume 0.43 cc. per g., specific surface 1.9 sq. m. per g.

Fig. 5 presents differential distribution curves for volumes of transitional pores according to their radius, instead of its logarithm. Curve 1 is derived from mercury pressure infiltration measurements, Curve 2 from capillary condensation of benzene vapor, measured without correcting for the amount adsorbed, and Curve 3 gives values corrected for the thickness and volume of the adsorption layers. Dzhighi's adsorption isotherm for benzene

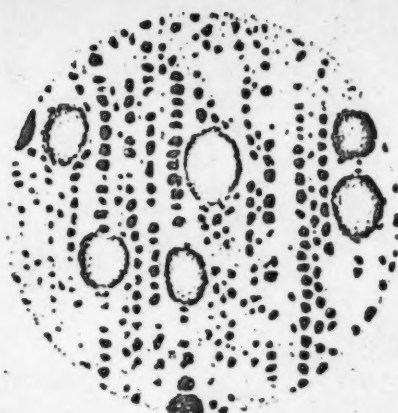


Fig. 1. Photomicrograph of wood charcoal.

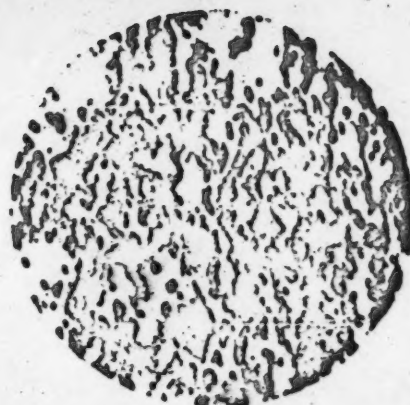


Fig. 6. Electron photomicrograph of silica gel E, shadowed with gold. The pores are seen as dark circles. Magnification 13,000.



Fig. 3. Electron photomicrograph of sugar charcoal with well developed porosity.

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vapor on lamp black consisting of spherical particles, and activated at 950° in vacuum, was taken for the calculation of the corrections; the adsorbent had a specific surface of 100 sq. m. per g., and from this the volume of the unimolecular adsorption layer was derived. The thickness h of the adsorption film is given for each equilibrium relative pressure by the quotient of the amount of vapor adsorbed and the amount needed for formation of a continuous adsorption monolayer.

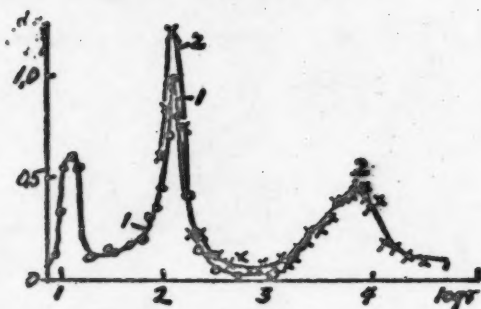


Fig. 4. Differential distribution curves for volumes of all varieties of pores of active charcoal according to logarithms of effective radii.

by Thomson's equation for the mean equilibrium relative pressure for the given interval.

The introduction of the correction for adsorbed vapor causes Curve 3 to have a shape similar to that of Curve 1, the position of the maximum being shifted by about 10 Å, being about 6% of the effective radius $\bar{r} + h = 154$ Å for the maximum of the curve. This divergence is not a significant one, and the coincidence between curves 1 and 3 may be considered as being satisfactory.

It may thus be said that active charcoals possess in general a tridisperse structure. For many specimens of charcoal the volume of transitional pores is exceedingly small (> 0.05 cc. per g), and these charcoals may be regarded as bi-disperse systems, possessing only two kinds of pores: macro- and micro-pores. On the other hand, in specimens of charcoal in which the activation process has been pushed to the limit, the size of micropores increases to that of transitional pores, while macropores becomes still larger than they were. We thus again have a bi-disperse system made up of transitional and macro-pores, with a negligibly small volume of micropores. As has been shown by Kiselev, for such adsorbents the specific surface of the pores s_p coincides with the specific area of the adsorption film s_a at the point at which hysteresis begins. It is obvious that this criterion excludes from consideration the surface of the micropores, if these are present, being fully filled by a purely adsorptional process before capillary condensation commences.

A detailed study of silica gels has been made in our laboratory by Kiselev, using a number of specimens specially prepared for the purpose by Nelmark. Pore dimensions were determined by the mercury pressure infiltration method by Kiselev and Kamakin.

A peculiarity of the silica gels, connected with the conditions under which they were prepared and in which their structure was formed is the practical absence of pores with diameters corresponding with the macropore class. Thus for the most coarse-pored of the gels studied, silica gel E, the volume of pores of radii exceeding 1000 Å is less than 0.05 cc. per g., as given by the mercury infiltration method. This volume is considerably smaller for the remaining, fine-pored gels.

For each interval of relative pressures along the desorption branch of the isotherm for sorption of benzene vapor by charcoal there corresponded an increment in the volume ΔW_1 of liquified vapor. This increment corresponded approximately to the area of the adsorption film $\Delta s = 2\Delta W_1/R$, which does not differ significantly for such coarse pores from the surface area of the filled pores for the given interval of relative pressures. The product $\Delta s h = w$ gave the volume of the adsorption film. The real volume of the pores ΔW , which is filled within the relevant interval of relative pressures, is expressed by:

$$\Delta W = \Delta W_1 + w - \Delta W_2 \quad (2)$$

where $\Delta W_2 = s_p \Delta h$ is a correction for the increase in volume of the adsorption film in the larger pores, having a specific surface s_p , determined by a thermodynamic method. The fraction $\Delta W'/(r + h)$ gave the differential volume of pores, corresponding to an effective radius $\bar{r} + h$, where \bar{r} was derived

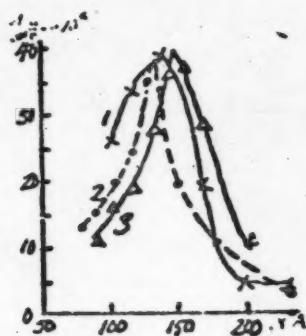


Fig. 5. Differential volume distribution curves for transitional pores of active charcoal according to their effective radii.

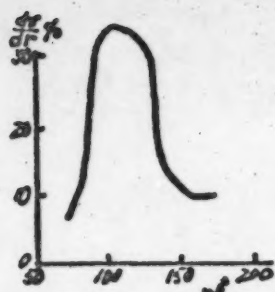


Fig. 7. Differential volume distribution curve according to pore radii for silica gel E, from electron microscope data.

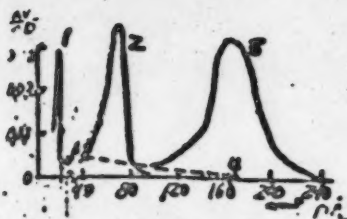


Fig. 8. Differential distribution curves for volume of pores according to their radii. Curve 1: silica gel A, Curve 2: silica gel K, Curve 3: silica gel E, and Curve 4: silica gel B.

their dimensions. A statistical treatment of a large number of such photomicrographs gives a differential curve for distribution of pore volumes according to their radii (Fig. 7). The maximum of this curve corresponds with effective pore radii of about 100 Å, which is in satisfactory agreement with the value derived from the capillary condensation theory.

The sorption measurements give the possibility of constructing more detailed distribution curves, given in Fig. 8, for a number of silica gels. These curves are derived from the theory of capillary condensation from the desorption branches of sorption isotherms of vapors. The abscissas of the graphs represent effective pore diameters in Å.

Silica gels 1, 2 and 3 belong to the class of uniform pore size sorbents. Curve 1 relates to the finest pore size silica gel A, most of the pores of which have an effective radius of 15 Å, belonging to the class of micropores. For silica gel K (Curve 2) the maximum of the distribution curve is for pores of effective radius ~40 Å. Such pores are close to transitional ones. Finally, for the most coarse-pored silica gel E (Curve 3) the maximum of the curve is at 90 Å, which is typical of transitional pore dimensions. Curve 4 (broken line) gives an idea of the structure of silica gel B with a mixed type of porosity.

We thus see that the pores of silica gels may belong to the classes of micro- and transitional pores. We did not encounter any specimens with well marked bi-disperse structure. There is obviously no reason why, in principle, such silica gels should not exist; such structures have been encountered among the porous glasses studied by Zhdanov.

The experimental data presented in this paper afford confirmation of the conceptions relating to types of pores of adsorbents, as developed by us, in particular for active charcoals, and they show the validity of the methods used for the determination of the volumes of each type of pore, and for their distribution according to pore radius. It should be noted that the terms micropore and macropore are also encountered in the foreign literature, where they are given an arbitrary significance, and express a qualitative picture intended to describe adsorbent structure.

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Silica gels possess either a uniform pore diameter, and belong in that case to the class of mono-disperse adsorbents, or they have a mixed type of porosity, with a broad gradation of pore diameters. The structure of the relatively coarse-pored silica gels may be observed directly by means of the electron microscope, and it may be studied by the methods of infiltrating mercury under pressure, or of capillary condensation of vapors.

The electron photomicrograph (Fig. 6), prepared by Radushkevich and Lukiyonovich, gives an idea of the uniformly coarse-pored silica gel E, for which the pores may be classified according to

Institute of Physical Chemistry
Academy of Sciences, U.S.S.R.

NATURAL SORBENTS OF THE FAR EAST. PART 2.
SORPTION OF BENZENE VAPOR BY NATURAL SORBENTS,
AND THE STRUCTURE OF SORBENTS

V. T. Bykov

We have for many years conducted a study of natural sorbents (decolorizing earths) with a view to their application in the oil industry for the purification of petroleum products, as well as for purification of products of semi-coking of coal, for regeneration of used petroleum lubricants, and for refining of soya bean, seal, and fish oils. These researches demonstrated the effectiveness as decolorizers of earths from a number of locations [1, 2, 3]. In view, however, of the diversity of the requirements of modern industrial practice for sorbents, the time has come to conduct a study of the internal structure of natural sorbents, to classify them according to their structural types, and to achieve a more profound knowledge of their properties, in order to arrive at a fuller and more rational utilization of such solvents in industry.

Natural sorbents are highly disperse bodies with a large internal surface ("specific surface") accessible to vapors and liquids, and attaining an area of the order of hundreds of square meters per gram of sorbent. The conditions under which they were formed, and the factors favoring formation of highly disperse substances in nature, are little known, and they require for their elucidation a systematic study of the properties of such sorbents. Such a study would, moreover, allow the most active ones to be recognized; it is known that certain natural sorbents are in no way inferior to artificially made ones [4].

The investigation of natural sorbents is more difficult than is that of artificial ones, such as charcoals, silica gels, and alumina gels. The natural sorbents are in most cases complex poly-mineral bodies, with diverse particle structures and surfaces. The structure of a natural sorbent plays a very important part in the sorption process. The internal structure of a sorbent is an important factor determining the velocity of sorption, the shape of the isotherm, and the magnitude of adsorption of molecules of the most diverse nature and structure [5, 6]. The geometric structure of an adsorbent, the size of its pores, their distribution according to size, and the heterogeneity of its surface are all factors affecting the magnitude of the adsorption potential. An increase in the adsorption potential, due to summation of attractive fields of opposite walls of the pores, takes place when the radii of the latter are of the same order of magnitude as the field. It is thus necessary, in the study of natural sorbents, to elucidate the structure of the skeleton of the sorbent, and of its pores, to determine the distribution of pore volume according to radius, and to find the nature of the solid-liquid or -vapor interface.

The structure of the skeleton of the sorbent is studied with the aid of the electron microscope and of X-ray analysis. The electron microscope study of natural sorbents allows one to draw conclusions regarding the degree of comminution of the natural product, the shape of its particles, and the mineral nature of the particles (crystals of kaolinite, gallusite, montmorillonite, etc.). The X-ray study of a homogeneous sorbent allows one to draw general conclusions regarding the presence of a given crystalline modification in the sorbent skeleton, to determine the crystalline parameters, and provides evidence concerning the mean degree of dispersion of the skeletal particles. The picture becomes a far more involved one in the case of poly-mineral sorbents, the X-ray analysis of which presents a problem of very great complexity. We have mostly applied the electron microscope method to the study of the skeleton of natural sorbents, as described in a previous paper [15].

We applied very delicate adsorptional methods to the study of pore structure and of distribution of pore volume according to diameter, for typical Far-Eastern natural sorbents. The use of adsorptional methods permitted of a more profound study of the nature of the processes taking place in the pores of a natural sorbent, and gave an insight into its structure.

The complex of measurements necessary in order to reveal the structural type of sorbent, the nature of distribution of pore volume according to radius, the magnitude of the specific surface of the sorbent skeleton, and the area of the adsorption film has been termed by Kiselev the adsorption-structural method for the study of highly disperse substances [7-9]. The study of the structure of a natural sorbent, and of the distribution of the volume of its pores according to radius is achieved by the use of adsorbates of different molecule size and structure, which penetrate to a greater or lesser amount into the pores, where they undergo adsorption. The development of such adsorption methods of study of structure may proceed in the following directions, for natural sorbents: (a) study of adsorption of gases and vapors, (b) study of adsorption from solutions, and (c) study of heat of adsorption of vapors and of heat of wetting of sorbents. In addition various methods for the study of macropores may be applied, such as that depending on their infiltration with liquids under pressure, and on electron microscope observation of the shape and dimensions of particles of the highly disperse substances.

In the study of adsorption of gases and vapors, the small molecules of gas penetrate into the finest pores of the sorbent, and an indication of the magnitude of the internal surface of the adsorbent is given by the amount of gas adsorbed. By determining adsorption of a series of gases and vapors of increasing molecule size an indication of diminishing accessibility of the internal surface is given. However, at saturation the internal surface of adsorbents is not fully covered by gas molecules, since only the active parts of this surface take part in the process, and it is hence preferable to apply the method of sorption of vapors to the study of porous bodies [8]. The results of the application of this method to the study of the structure and properties of natural sorbents are presented in this paper.

The method depending on study of adsorption of dissolved substances also permits one to draw conclusions regarding diminishing accessibility of the adsorbent surface as solute molecule size increases. This method of "molecular probes", supplementing that of sorption of vapors, leads to the characterization of the structure of the adsorbent. The method of adsorption from solutions is more limited in its application than is that of adsorption of vapors, since in the former case complications due to competition between solvent and solute molecules for the adsorbent surface enter. We did not use the methods depending on determination of heats of adsorption of vapors or of wetting of the adsorbent.

Methods Used for Study of the Structure of Natural Sorbents

A vacuum apparatus with quartz balances, was constructed along the lines of that described by Chmutov [5], with certain modifications, as shown in Fig. 1. The apparatus was designed for the study of the sorbent properties of natural sorbents, by the method of sorption of vapors, in the Sorption Processes Laboratory, Institute of Physical Chemistry, Academy of Sciences, U.S.S.R.

The vacuum apparatus possesses four sorption tubes 1, within which are suspended calibrated quartz spirals 2, from hooks forming part of the ground glass stoppers, which are used without grease, being sealed with mercury. The cups 3 containing weighed amounts of natural sorbent were suspended by glass threads from the quartz spirals. The sorption tubes were connected with two MacLeod mercury manometers 4 and 5, covering the range 8.67×10^{-6} to 7.44×10^{-1} mm. and with a U-shaped mercury manometer 6, permitting, with the aid of a cathetometer with a reading microscope, of the measurement of vapor pressure, up to saturation, and then with a Bauer valve for the introduction of vapor 7, with an applicator tube 8. The instrument is then connected through a U-shaped safety tube 10 through tap 11 to a Langmuir mercury diffusional three-stage pump 12 with a pre-vacuum system.

The measurements are made as follows: portions of 70-100 mg of air-dry or dried natural sorbents are weighed out in weighed cups. In most cases the sorbents were powdered and passed through a sieve with 6400 apertures per sq. cm. The cups, containing portions of natural and standard sorbents, are suspended in the sorption

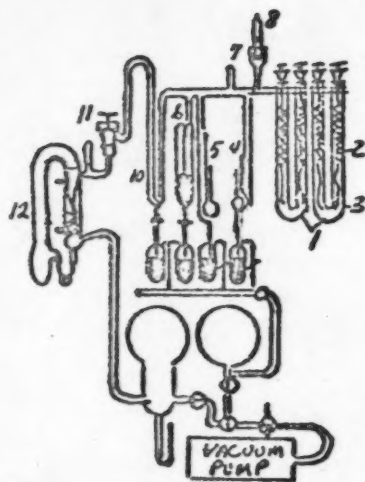


Fig. 1. Vacuum apparatus for study of sorption.

tubes, and the mercury seals are applied to the cocks. The initial position of an indicator on the glass threads is read with the aid of a cathetometer fitted with a microscope, on a scale placed within the sorption tubes.

An electric heater is placed under the sorption tubes, and air is pumped out, at first using the low-vacuum pump, and then the mercury diffusion pump 12, with the lower part of the sorption tubes at 200°. Evacuation is continued until the pressure falls to 10^{-5} mm. Tap 11 is then closed, and heating is discontinued; the heater is removed during the cooling process, and the position of indicators on the glass threads is read on fixed scales within the tubes.

The loss of weight of the sorbents indicates removal of moisture and gases. Further calculations are now based on the dry weight of the sorbents. The lower parts of the tubes are now immersed in a water thermostat at 20° (this was taken as the standard temperature for all our measurements). A small amount of vapor is now introduced into the system, by contacting for a short time the porous membrane of applicator tube 8 (containing degassed liquids, such as benzene, methanol, etc.) with a porous diaphragm of funnel 7. Slight elevation of the tube 8 allows a layer of mercury to separate the membranes, so preventing further diffusion of vapor into the vacuum system.

After establishment of equilibrium, as shown by cessation of movement of the pointers on the glass threads and by achievement of constant pressure, the displacement of the pointers is read off on the scales, which are graduated in 0.01 mm. The equilibrium vapor pressures are read on the MacLeod manometers 4 and 5 and the mercury manometer 6, with the aid of a cathetometer. A fresh portion of vapor is then introduced, and readings are again taken after establishment of the new equilibrium. These manipulations are continued until full saturation of the sorbent is achieved. The lower part of the U-shaped safety tube 10 is filled with mercury in order to protect the grease of tap 11 from the action of the vapors.

The desorptional branch of the isotherm is obtained by measuring equilibrium pressure and loss of weight of sorbent following progressive lowering of pressure obtained by opening tap 11 so as to connect with the low vacuum system. The establishment of equilibrium during desorption takes place very slowly; several days may be needed to obtain one point on the isotherm. The sorption and desorption isotherm measurements were usually repeated 2-3 times, from a high vacuum to full saturation, and back again. In addition to this, control measurements were made, involving comparison with standard sorbents. In order to increase the accuracy of the measurements the whole apparatus was placed in an air thermostat, in addition to keeping the lower parts of the sorption tubes in a water thermostat.

We initially took measurements of sorption of methanol vapor, but the majority of natural sorbents exhibit swelling of the skeleton and show that a chemisorptive process has taken place [7]. We therefore abandoned work with methanol, and concentrated on measurement of sorption of benzene vapor. The work of the sorption apparatus was checked by reference to a standard sorbent AC(II), for which trustworthy adsorption isotherms for benzene vapor had been derived in Dubinin's laboratory.

Checking and calibration of the quartz spirals were systematically performed during the course of the experiments.

Experimental Data on Sorption and Desorption of Benzene Vapor by Natural Sorbents

Two or more samples of each natural sorbent were taken from each of the more important deposits, preferably from those parts which were under exploitation or were suitable for exploitation. The degree of weathering of the tuffs from each particular location varies to some extent within it, and the sorptive properties will obviously also vary accordingly. It was for this reason desirable to take samples of the actual product being dug up and transported from the site.

Sorption and desorption isotherms for benzene vapor were derived for samples of ashy liparite tuffs and their weathering products. These minerals are of noogene origin, and they belong to the so-called Suyfun deposit [10]. They are represented in this paper by samples No. 17, 18, 19, and 135 (ashy tuffs), and Nos. 20, 124, 127, and 130 (weathered ashy tuffs).

Many of the natural sorbents studied were products of weathering of agglomerative tuffs from early quaternary volcanoes [11, 12]; the samples studied were Nos. 81, 92, 93, 86, 87, 88, 95 and 96. In addition we studied the diatomaceous earths Nos. 81, 82, 29, 101, and 142. In order to compare the properties of the basic group of Far Eastern natural adsorbents with their more important counterparts from the European U.S.S.R. we obtained the

benzene vapor, and desorption of benzene vapor by ashy tuffs and bleaching earths at 20°

Table 1 gives the amount of sorbed benzene in millimoles per gram of sorbent for different pressures of benzene vapor and equilibrium times for the specific surface of the sorbent skeleton and for the area of the adsorption film. The determination of the specific surface of the sorbent skeleton was performed by the method of Brunauer, Emmett and Teller [13] and of the area of the adsorption film by Kiselev's method [14].

TABLE 1
Sorption of Benzene Vapor by Natural Sorbents

Description of samples and specimens	Point of sorption, °C	Volume of sorbed benzene, mm ³ /g × 10					Specific surface	
		At the point of beginning of sorption	At the point of beginning of desorption	At p/p ₀ = 0.25	At p/p ₀ = 0.5	At p/p ₀ = 0.75	At full saturation	Of the skeleton S _{sk} in m ² /g Of the adsorption film S _{af} in m ² /g
Ashy tuff	17 0.15	13	16	32	81	141	26	19
	18 0.15	18	27	37	80	136	40	27
	175 0.20	18	22	41	100	147	34	29
Weathered tuff	20 0.15	14	27	46	90	102	(27)	39
	124 0.17	18	34	58	119	143	40	(45)
	130 0.16	17	35	58	123	147	38	(55)
Agglomerative tuff	81 0.50	9	8	9	55	88	14	8
	170 0.24	11	13	14	26	29	12	—
	122 0.16	38	48	55	202	255	77	77
Weathered	175 0.30	44	39	55	155	290	76	—
	123 0.15	14	20	39	169	209	(32)	48
	16 0.16	25	36	54	121	220	46	40
	15 0.15	31	55	75	131	162	57	49
	11 0.18	40	51	82	14	135	70	51
	12 0.15	16	32	51	88	222	42	—
	91 —	—	31	61	178	248	82	—
	80 0.14	41	76	118	208	212	85	83
	87 0.18	25	38	59	214	369	40	53
	88 0.20	53	112	169	700	844	155	132
	14 0.20	76	87	167	688	866	154	150
	81 (0.22)	(19)	18	31	82	323	26	14
Diatomaceous earths	82 (0.23)	(24)	—	—	—	373	33	18
	95 0.18	17	21	31	82	125	33	8
	101 0.14	18	30	42	80	175	34	29
Industrial bleaching earths	142 0.23	18	19	27	104	176	29	16
	—	—	—	—	—	—	—	—
Fuller's earth	30 0.175	46	55	105	309	446	88	(16)
Activated carburene	71 0.175	36	56	102	206	223	68	72
Wash line 6	74 0.18	32	35	54	430	503	53	(65)
Wash line C	73 0.17	54	66	97	182	208	87	52
Opab	75 0.27	53	50	93	130	140	83	34

All the sorption isotherms obtained for natural sorbents are S-shaped, as can be seen in Figs. 2-9, in which the ordinates represent amounts of sorbed (rings) or desorbed (circles) benzene vapor, in millimoles per gram of sorbent, while the abscissas are equilibrium relative pressures. An analysis of the sorption isotherms suggests a relatively modest sorption of benzene vapor by ashy tuff tuffs (samples No. 17, 18 and 11) using for medium data at 20° for weathered tuffs (Nos. 20, 124 and 130) as appears from the Table and from Figs. 2 and 4. The specific surface of ashy tuffs varies from 25 to 35 m²/g, and for weathered ashy tuffs from 10 to 40 m²/g.

Weathered agglomerative tuffs have a much greater sorbent power. The original volcanic agglomerative tuffs in their natural unweathered state (samples No. 84 and 171) gave only small sorption values amounting at saturation to 0.083-0.002 cc/g, and they had small specific surface values of 14-12 sq. m. per g. The products

of weathering of agglomerative tuffs have good adsorbent properties with elevated values for adsorption at low and

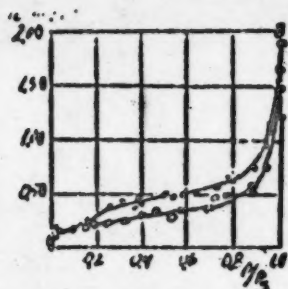


Fig. 2. Sorption and desorption isotherm for benzene vapor on ashy tuff (sample No. 18).

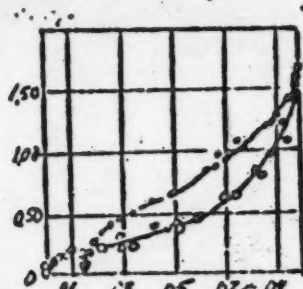


Fig. 3. Sorption and desorption isotherm for benzene vapor on weathered ashy tuff (sample No. 130).

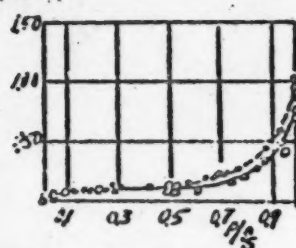


Fig. 4. Sorption and desorption isotherm for benzene vapor on agglomerative tuff (intact, sample No. 84).

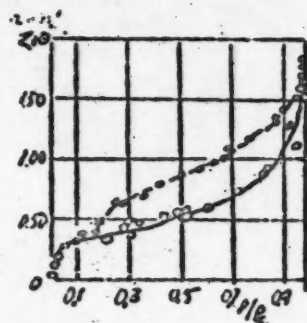


Fig. 5. Sorption and desorption isotherm for benzene vapor on agglomerative weathered tuff (sample No. 95).

A number of samples of diatomaceous earths (samples No. 99, 101 and 142) exhibit sorbent properties of the same order as liparite ashy tuffs and their weathering products. However, samples of diatomaceous earth from one location (Nos. 81 and 82) had a very high sorptive capacity attributable to capillary condensation at high degrees of saturation, which is evidence of the relatively coarse pores of these samples. These sorbents should therefore be suitable for purification of heavy petroleum products from which large molecule size admixtures are to be removed.

The active natural sorbents studied by us for purposes of comparison, and which include the most important bleaching earths of the U.S.S.R., are characterized by the steep rise in the isotherm at the point of beginning of hysteresis, where adsorption amounts to 0.4-0.6 mm/g, or 0.030-0.050 cc/g, with a considerable part of the sorption being due to capillary condensation, leading at saturation to sorption of 0.20-0.50 cc/g. All the highly active natural sorbents are characterized by a diffuse distribution of pore volume according to radius, with a considerable fraction of coarse pores.

The comparison of these with the Far Eastern sorbents shows that the isotherms for a series of agglomerative weathered tuffs are close to and similar to those for Gumbrine, Gilyah, and Fuller's earth. This similarity of isotherms reflects a similarity of structures of these natural sorbents and suggests that they have similar adsorptive properties. The agglomerative tuffs in many cases exhibit high sorptive activity, and they should be useful as bleaching earths for mineral and vegetable oils.

of weathering of agglomerative tuffs have good adsorbent properties with elevated values for adsorption at low and medium saturations, and with the amount of benzene sorbed at full saturation 2-3 times greater. The specific surface is 5-6 times greater, attaining values of 70-80 sq. m. per g. The separate inclusions of argillaceous minerals formed during weathering of agglomerative tuffs have a high adsorbent activity. Thus, for example, sample No. 88 (magnesian montmorillonite from inclusions in agglomerative tuff) gives a limiting sorption of benzene equal to 0.844 cc/g, and has a specific surface equal to 155 sq. m. per g, i.e., its adsorptive properties exceed those of some artificial adsorbents. Similar high activity is shown by montmorillonite from another location (sample No. 94).

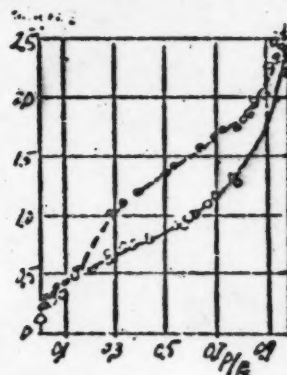


Fig. 6. Sorption and desorption isotherm for benzene vapor on agglomerative weathered tuff (sample No. 86).

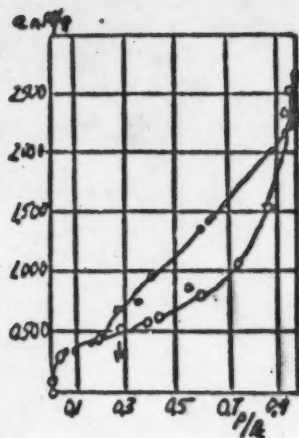


Fig. 7. Sorption and desorption isotherm for benzene vapor on activated gum-brine (sample No. 71).

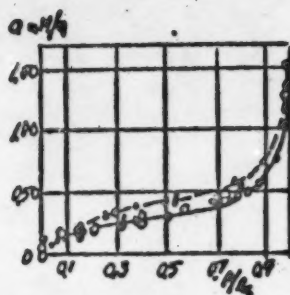


Fig. 8. Sorption and desorption isotherm for benzene vapor on diatomaceous earth (sample No. 101).

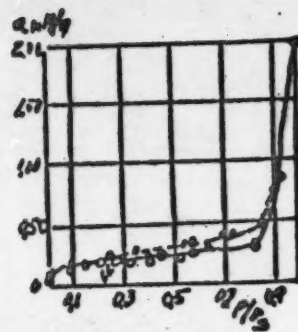


Fig. 9. Sorption and desorption isotherm for benzene vapor on diatomaceous earth (sample No. 142).

SUMMARY

1. Sorption and desorption isotherms for benzene vapor on natural sorbents from a number of deposits have been constructed, and have been compared with isotherms for some of the more important natural sorbents taken from European parts of the U.S.S.R.
2. Certain of the sorbents exhibited high sorptive capacity, and had structures and properties similar to those of gum-brine, Nalchikines, and Fuller's earth.

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Laboratory of Sorptional Process
Institute of Physical Chemistry
Academy of Sciences, U.S.S.R.

ROLE OF INERT DILUENTS ON CATALYTIC DEHYDROGENATION OF ETHYLBENZENE

N. I. Shulkin and I. I. Levitsky

Numerous papers on catalytic dehydrogenation of ethylbenzene to give styrene have been published during the past decade. A well known method of raising the styrene content of the catalyzates depends on dilution of the ethylbenzene with inert gases (CO_2 , N_2 , steam) [1,2]. This effect is explained [1,3,4] as being due to lowering of the velocity of the side reaction of cracking and polymerization of styrene, due to lowering of the concentration of the latter in the vapor phase.

The method of kinetic determination of relative adsorption coefficients was applied in one of the papers cited [4] to the study of the effect of carbon dioxide on the dehydrogenation of ethylbenzene. It was found that the styrene content of the catalyzates rose from 33 to 56.3% as the carbon dioxide content of the reaction mixture rose from 0 to 88%. The author comes to the conclusion that the adsorption coefficient of carbon dioxide is equal to zero, and that the depth of dehydrogenation of ethylbenzene remains constant, and is not affected by dilution with carbon dioxide. The increased yields of styrene are ascribed to inhibition of polymerization; no numerical data in support of these views are presented, however.

Marukyan [5] and Tolstopyatova [6] found that depth of dehydrogenation of ethylbenzene rises as it is diluted with xylenes, toluene, or benzene, and falls with increasing styrene content. The authors ascribe these effects to the circumstance that the adsorption coefficients of xylenes, toluene, and benzene are considerably lower, and of styrene higher, than is that of ethylbenzene. These results, moreover, led to the derivation of "a generalized kinetic equation for catalytic unimolecular reactions at homogeneous surfaces in a flowing system, allowing for displacement by other substances present" [6]. The role of inert gases and hydrocarbons is thus believed by the above authors to be due exclusively to kinetic factors.

The role of inert diluents may, however, be of an entirely different nature, if the reaction of dehydrogenation of ethylbenzene has under the given conditions been able to approach or reach a state of thermodynamic equilibrium:



This reaction proceeds with increase in volume, for which reason inert diluents should, in the same way as lower pressures, cause lowering of the partial pressures of the components of the equilibrium mixture, and hence shift the equilibrium in the direction of styrene production.

Mitchell [7] has already expressed a similar opinion on the role of steam in the dehydrogenation of ethylbenzene, without, however, advancing any experimental or numerical data in support of it.

The object of the research described in this paper was to find how close the product of dehydrogenation of ethylbenzene over catalysts of ordinary activity is to the composition of the thermodynamic equilibrium mixture, and to find whether addition of inert diluents shifts the equilibrium towards higher styrene production.

EXPERIMENTAL

Research Methods

Apparatus. The reactor was a quartz tube of internal diameter 20 mm placed in an electric oven 90 cm long, which maintained a uniform constant temperature over a length of 40 cm. The supply of current to the oven was controlled by a thermo-regulator with a mercury relay, the fluctuations in temperature not exceeding $\pm 1^\circ$. Temperatures were measured by a compensations' method, using a chromium-aluminum thermocouple, which was carefully calibrated. The thermocouple was placed within a porcelain sleeve situated in the middle of the catalyst

After the reaction tube was connected with a three-way tube, serving for introduction of ethylbenzene from an external source, of the distillation, and of the thermocouple leads. The distal end of the tube was connected with a receiver cooled in ice.

The catalyst, containing 10% of sodium, differed very little in stability and activity from Marukyan's [5] copper-chromium catalyst. All the experiments described were performed with a single specimen of catalyst, with a volume of 50 ml.

Analysis. The styrene content of the catalysts was determined by bromometric titration by Rosenmund's method [9]. The analyses were performed immediately after each experiment, since the styrene content changes significantly when the catalysts are stored.

Performance of the experiments. The catalyst was regenerated after each experiment by passing through it a current of air at 575-600° for 90 minutes. The initial activity of the catalyst was thus maintained throughout our experiments. After regeneration the reaction tube was swept out with a stream of nitrogen or carbon dioxide, after which we began the introduction of a stream of the gas (nitrogen or hydrogen) in presence of which the given experiment on dehydrogenation of ethylbenzene was being conducted; the flow of gas was regulated by means of a rheometer. All experiments were conducted at 575°, the temperature being raised initially to about 585°, so that the actual dehydrogenation took place at 574-576°. Four to eight ml of ethylbenzene were then introduced, at an appropriate rate, and the experiment was commenced when conditions had become stabilized, when the receiver was changed. A total of 8-15 ml of ethylbenzene or of its mixtures with toluene was passed through the tube.

Substances. The ethylbenzene, after being boiled over sodium, had the following constants: b.p. 135.9-136.1°, n_D^{20} 1.4966, d_4^{20} 0.8664. The toluene was distilled from sodium; it had b.p. 110.5-111.0°, n_D^{20} 1.4960, and d_4^{20} 0.8662. The hydrogen used as a diluent was first passed through a red-hot quartz tube containing freshly reduced copper, and then through a calcium chloride tube and a rheometer, before entering the reaction tube. Hydrogen was first passed through a tube containing granulated charcoal, then over calcium chloride, and then through a flow meter to the reaction tube.

Dehydrogenation of Undiluted Ethylbenzene

Dehydrogenation in absence of diluents was studied at different molar flow velocities, given in the Tables as moles of substance passed per hour through 1 liter of catalyst; the corresponding volume velocities are expressed in liters per hour per liter of catalyst.

TABLE 1
Dehydrogenation of Ethylbenzene without Diluents

No. of Experiment	Volume velocity	Volume velocity	Yield of catalyst, % of ethylbenzene passed	Styrene content of the catalyst, as % by weight
1	2	3	4	5
2	0.30	2.4	88	18.6
3	0.63	5.2	91	23.1
4	1.04	8.6	94	24.8
5	1.26	9.9	94	25.4
7	1.47	12.1	95	26.3
34	1.77	14.6	96	24.3
6	1.91	16.0	97	25.4
35	2.40	19.8	94	24.7

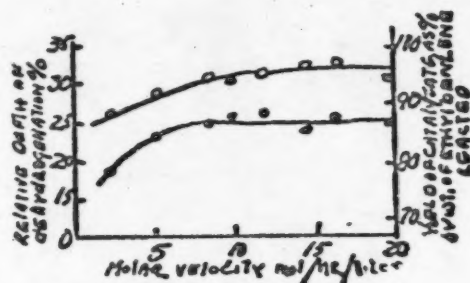


Fig. 1. Dehydrogenation of ethylbenzene without diluents: ● = relative % dehydrogenation; ○ = yield of catalyst.

A rise in the molar velocity of ethylbenzene from 2.4 to 8.6 leads to a rise in the styrene content of the catalyst, from 18.6 to 24.8%. It may be supposed that polymerization of the styrene produced varies parallel with duration of contact with the catalyst. This explanation is confirmed by a corresponding increase in the yield of catalyst from 88 to 94%.

Further increase in molar velocity from 8.6 to 19.8 has no further effect on the yields of catalyzate, or on its styrene content. This constancy of the relative depth of dehydrogenation of ethylbenzene, and its independence of duration of contact may be due to the reaction attaining thermodynamic equilibrium. The independence of the yields of catalyzates and of the relative depths of dehydrogenation (taken as being equal to the styrene content of the catalyzates) of molar velocity is illustrated by the curves of Fig. 1.

The constant depth of dehydrogenation of ethylbenzene at different molar velocities has already been reported by other workers. Marukyan [8] obtained the same yields of styrene from 1:2 ethylbenzene vapor-carbon dioxide mixtures at 600°, when the molar velocity was varied from 8.2 to 22.4. It may be supposed that side-reactions could not significantly affect the constancy of the depth of dehydrogenation. The pyrolysis of ethylbenzene and styrene, and the polymerization of the latter have been studied by Marukyan and Tolnopyatova [10] for flowing systems; they found that variations in duration of contact did not cause any considerable change in the extent to which these reactions proceeded. Thus at 575°, with a time of contact of 155 sec. 5.9% of the styrene was decomposed, as compared with 3.0% for 77 or 31 sec.

It is quite obvious that the actual depth of dehydrogenation of ethylbenzene was somewhat more than the values found by us. The temperature of our experiments was such as would involve the reactions of cracking and polymerization. The depth of dehydrogenation at equilibrium calculated by us from free energy and heat content functions was found to be 34% at 575°, which exceeds the experimental value by about 9%. This difference is somewhat greater than the value for losses (cf. Column 4, Table 1) due chiefly to polymerization of styrene.

Dehydrogenation of ethylbenzene mixed with hydrogen, nitrogen, or toluene was studied at molar velocities of 8.6-19.6. It was of interest to compare the experimental results with those derived from thermodynamic calculations based on our experimental results, instead of on the values given by spectrum analysis. Agreement between calculated and experimental results would be decisive evidence in favor of the existence of a dynamic equilibrium. For the calculation of the equilibrium constants of the reaction we took the value of 25% for the relative equilibrium depth of dehydrogenation of ethylbenzene in the absence of a diluent; this value is the mean of those obtained in experiments 4-7, 34, and 35 (Table 1).

The thermodynamic calculations of all the experiments of this research were made with the aid of the well known equation [11] (compare with [12]), which for the reaction



has the form

$$K_p = K_n \left(\frac{P}{n_B + n_C + n_R + n_S + n_{in}} \right)^{(r+s)-(b+c)} \quad (1)$$

Here

$$K_p = \frac{P_R^r P_S^s}{P_B^b P_C^c}$$

where $P_{R,S,...i}$ is the partial pressure of the i -th reacting component, $n_{R,S,...i}$ is the number of moles of the i -th component in the equilibrium mixture, n_{in} is the number of moles of inert diluent present in the equilibrium mixture,

$K_n = \frac{n_R^r n_S^s}{n_B^b n_C^c}$, and P is the external pressure.

For the reaction $\underset{1}{C_6H_5-CH_2-CH_3} = \underset{2}{C_6H_5-CH=CH_2} + \underset{3}{H_2}$, conducted at atmospheric pressure without dilution,

and for dehydrogenation of 1 mole of ethylbenzene with production of x moles of styrene the separate terms of equation (1) will be equal to: $n_1 = 1 - x$

$$n_2 = n_3 = x; P = 1; n_{in} = 0; (r + s) - (b + c) = 2 - 1 = 1.$$

Substitution of these values in equation (1) gives

$$K_p = \frac{n_2 n_3}{n_1 (n_1 + n_2 + n_3)} = \frac{x^2}{(1-x)(1+x)} = \frac{x^2}{1-x^2} \quad (2)$$

The depth of dehydrogenation at equilibrium was taken as 25.0%, whence $x = 0.25$, the substitution of which in equation (2) gives $K_p = 0.0667$. All further thermodynamic calculations were based on the value of K_p so found.

Dehydrogenation of Ethylbenzene Vapor Diluted with Hydrogen

Addition of hydrogen should shift equilibrium in the direction of diminution of dehydrogenation, and should lead to a lowering of the styrene content of the catalyzates. Percentage conversion of ethylbenzene into styrene will then be determined by the degree of dilution with hydrogen. The depth of dehydrogenation calculated on the basis of the above-derived equilibrium constant should coincide with the experimental values under two conditions: (a) the reaction actually attains equilibrium, and (b) the depth of the side reactions of polymerization and cracking remains constant whether or not a diluent is used. In this series of experiments we wished to elucidate the effect of dilution with hydrogen on dehydrogenation of ethylbenzene, and to ascertain whether the calculated results coincide with the experimentally found ones.

In the dehydrogenation of 1 mole of ethylbenzene, with production of x moles of styrene, and with dilution of each mole of ethylbenzene with m moles of hydrogen, the equilibrium mixture will have the composition: $n_1 = 1-x$; $n_2 = x$; $n_3 = x + m$. Substituting these expressions in the left-hand side of equation (2) we obtain:

$$K_p = \frac{n_1 n_2}{n_1(n_1 + n_2 + n_3)} = \frac{x(x+m)}{(1-x)(1+x+m)}$$

which after simple transformations gives

$$(1 + K_p)x^2 + (m + K_p m)x - K_p(1 + m) = 0 \quad (3)$$

The results of all the experiments of this series are calculated from equation (3). The degree of dilution of ethylbenzene with hydrogen, m , was determined by dividing the molar velocity of hydrogen by that of ethylbenzene.

The results obtained are presented in Table 2 and the values of columns 11 and 12 are shown in the graph of Fig. 2 (lower curve). The styrene content of the catalyzates fall with increasing dilution from 23.2 to 10.2%. For all ethylbenzene-hydrogen ratios studied the calculated values were 3.0-4.5% lower than the experimental ones; the deviations are shown in the last column of Table 2. These deviations could be predicted, as being a result of inhibition of the reaction of polymerization of styrene, with consequent raising of the yield of the latter. However, the small and practically constant value of the deviations suggests that the reactions had attained equilibrium.

The yields of catalyzate obtained, as percentage of ethylbenzene introduced*, are somewhat higher than found for experiments without diluent (compare column 10, Table 2 with column 4, Table 1); this testifies to lowering of depth of side reactions in systems diluted with hydrogen.

Dehydrogenation of Ethylbenzene Vapor Diluted with Nitrogen

We next investigated whether dilution with nitrogen was analogous to conducting the reaction at reduced pressure. Given degrees of dilution with nitrogen should, similarly to given reductions in pressure, lead to the obtaining of yields of styrene such as could be calculated from equation (1). Should calculated and experimental results be in agreement this would afford additional evidence of the attainment of an equilibrium state.

In the dehydrogenation of 1 mole of ethylbenzene with production of 1 mole of styrene, the ethylbenzene

* This refers to the amount of ethylbenzene passed over the catalyst during the experiment.

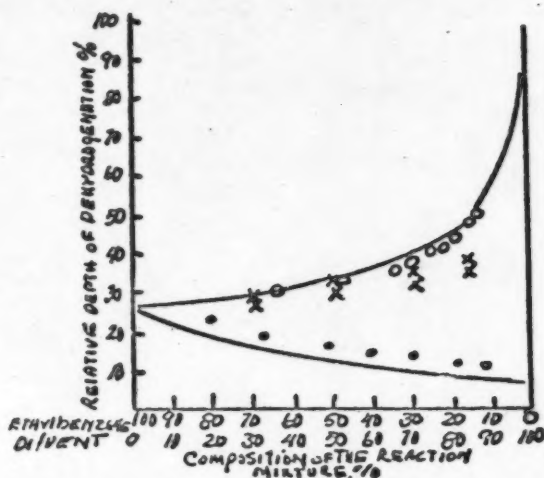


Fig. 2. Dehydrogenation of ethylbenzene diluted with hydrogen, nitrogen and toluene: lower curve - calculated from equation (3) for hydrogen; upper curve - calculated from equation (4) for inert diluents (o - for nitrogen, x - for toluene, • - for hydrogen).

TABLE 2
Dehydrogenation of Ethylbenzene Vapor Diluted with Hydrogen

No.	Volume velocity of ethylbenzene	Velocity of hydrogen in 1/hr (NTP)	Molar velocity			Molar composition of the mixture, %		Degree of dilution m	Yield of catalytic as % of ethylbenzene introduced	Depth of dehydrogenation, %		Deviation
			Ethylbenzene	Hydrogen	Total	Ethylbenzene	Hydrogen			Styrene content of catalyst	Calculated from eq.(3)	
1	2	3	4	5	6	7	8	9	10	11	12	13
29	1.24	2.8	10.2	2.5	12.7	80.3	19.7	0.25	96	23.2	19.6	+3.6
30	1.21	5.5	10.0	4.9	14.9	67.2	32.8	0.49	97	18.7	14.7	+4.0
31	0.92	8.2	7.6	7.3	14.9	51.0	49.0	0.96	97	16.0	11.5	+4.5
32	0.60	8.2	4.9	7.3	12.2	40.0	60.0	1.5	96	14.6	9.8	+4.6
33	0.64	13.8	5.3	12.3	17.6	30.0	70.0	2.3	97	12.7	8.6	+4.1
28	0.32	13.8	2.7	12.3	15.0	17.8	82.2	4.6	93	11.5	7.5	+4.0
27	0.17	13.8	1.4	12.3	13.7	10.5	89.5	8.5	93	10.2	7.1	+3.1

being initially diluted with n_{in} moles of nitrogen (or other inert diluent) per mole of ethylbenzene, the mixture of components of the equilibrium mixture with diluent will have the composition (see above): $n_1 = (1-x)$; $n_2 = n_3 = x$ and n_{in} . Substituting these expressions into equation (1), and on condition that $P = 1$, we obtain:

$$K_p = \frac{n_2 n_3}{n_1 (n_1 + n_2 + n_3 + n_{in})} = \frac{x^2}{(1-x)(1+x+n_{in})}$$

A series of simple transformations of this equation leads to

$$(K_p + 1)x^2 + K_p n_{in} x - K_p (n_{in} + 1) = 0 \quad (4)$$

All further calculations are made by substituting in equation (4). The dilution n_{in} was derived by dividing the molar velocity of nitrogen by that of ethylbenzene.

TABLE 3
Dehydrogenation of Ethylbenzene Vapor Diluted with Nitrogen

No.	Volume velocity of ethylbenzene	Velocity of nitrogen in 1/hr (NTP)	Molar velocity			Molar composition of the initial mixture, %		Degree of dilution n_{in}	Yield of catalytic as % of ethylbenzene introduced	Depth of dehydrogenation, %		Deviation
			Ethylbenzene	Nitrogen	Total	Ethylbenzene	Nitrogen			Styrene content of catalyst	Calculated from eq.(4)	
1	2	3	4	5	6	7	8	9	10	11	12	13
24	1.04	5.2	8.6	4.7	13.3	64.6	35.4	0.55	91	29.5	29.5	0
23	0.98	9.6	8.1	8.6	16.7	48.5	51.5	1.1	87	32.2	32.9	-0.7
16	0.41	7.6	3.4	6.8	10.2	33.5	66.5	2.0	87	36.4	37.5	-1.1
22	0.68	14.0	5.6	12.5	18.1	30.9	69.1	2.2	79	37.1	38.4	-1.3
18	0.50	14.0	4.1	12.5	16.6	24.7	75.3	3.0	75	41.7	41.6	+0.1
21	0.48	14.0	4.0	12.5	16.5	24.2	75.8	3.1	74	41.7	41.9	-0.2
20	0.39	14.0	3.2	12.5	15.7	20.4	79.6	3.9	71	43.3	44.4	-1.1
26	0.28	14.0	2.4	12.5	14.9	16.1	83.9	5.3	67	48.1	48.3	-0.2
19	0.24	14.0	2.0	12.5	14.5	13.8	86.2	6.2	65	49.5	50.4	-0.9

The results are given in Table 3, the values of Columns 11 and 12 being taken for the upper curve of Fig. 2. The difference between calculated and experimental values for depth of dehydrogenation does not exceed 1.3% (last column). This good agreement is strong evidence that the reaction has attained a state of thermodynamic equilibrium. The increased yields of styrene obtained when the ethylbenzene is diluted with inert gases (nitrogen, carbon dioxide, steam) are therefore ascribable to displacement of the equilibrium point in the direction of greater dehydrogenation, and not to the decreased velocity of side reactions.

It is of interest that the differences between calculated and experimental values are greater with hydrogen (3.0-4.5%) than with nitrogen (up to 1.3%). The depth of the reaction of polymerization of styrene is smaller in presence of hydrogen than in absence of a diluent, and this is ascribable to two factors: the fall in the yields of styrene, and its dilution with hydrogen. These factors act in opposite directions when the diluent is nitrogen; increase in the yields of styrene raises the velocity of the polymerization-reaction, while dilution with nitrogen reduces it. As a result, the depth of polymerization of styrene is practically the same with nitrogen as a diluent as without diluent.

The figures of Column 10, Table 3, are of interest. They show that the yield of catalyzate falls from 91 to 65% as dilution with nitrogen increases, whereas comparable dilutions with hydrogen gave consistently high and practically constant yields (93-97%). This effect may be connected with the high thermal conductivity of hydrogen, which is 7 times greater than that of nitrogen [13]. Under conditions in which ethylbenzene and styrene would have had time to condense from a hydrogen atmosphere, a stream of nitrogen would have carried some of the catalyzate from the receiver.

Dehydrogenation of Ethylbenzene - Toluene Mixtures

It was remarked in the introduction to this paper that the rise in depth of dehydrogenation of ethylbenzene due to dilution with toluene has been explained [6] as being a consequence of differences between adsorption of ethylbenzene and toluene at the active centers of the catalyst. The adsorption factor cannot, however, have any significance if the reaction has attained thermodynamic equilibrium; at this point toluene would act as an inert diluent, which shifts the position of the equilibrium point. Equal dilutions of ethylbenzene with nitrogen or toluene should in that case give equal yields of styrene.

The results of dehydrogenation of 4 ethylbenzene-toluene mixtures, containing 30, 50, 70, and 85 mol-% of toluene, are given in Table 4. Molar velocity was calculated from the volume velocity and the density of the mixtures, on the assumption that density follows the addition rule. The depth of dehydrogenation was calculated from the expression $100a/b$, where a is the styrene content of the catalyzate, and b is the ethylbenzene content of the original mixture. The results are shown in Column 11 of Table 4, and by the upper curve of Fig. 2.

TABLE 4
Dehydrogenation of Ethylbenzene Mixed with Toluene

No.	Composition of initial mixture				Volume velocity of mixture	Molar velocity of mixture	Degree of dilution n_{in}	Yield of catalyzate, as % of mixture introduced	Styrene content of catalyzate, as % by weight	% dehydrogenation of ethylbenzene		Difference
	% by weight Ethylbenzene	% by weight Toluene	mol-% Ethylbenzene	mol-% Toluene						Found	Calc. from equa. (4)	
1	2	3	4	5	6	7	8	9	10	11	12	13
8	73.0	27.0	70.0	30.0	1.14	9.8	0.43	94	20.0	27.4	28.6	-1.2
9	73.0	27.0	70.0	30.0	2.02	17.3	0.43	95	20.3	27.8	28.6	-0.8
10	53.3	46.7	50.0	50.0	1.67	14.6	1.0	94	16.7	31.4	32.4	-1.0
11	53.3	46.7	50.0	50.0	2.09	18.3	1.0	96	16.3	30.6	32.4	-1.8
13	33.0	67.0	30.0	70.0	1.84	16.8	2.3	96	11.0	35.2	38.7	-3.5
15	33.0	67.0	30.0	70.0	2.40	21.7	2.3	96	11.4	34.6	38.7	-4.1
36	17.0	83.0	15.1	84.9	1.62	15.0	5.6	97	6.3	37.0	49.1	-12.1
37	17.0	83.0	15.1	84.9	2.16	20.0	5.6	97	6.3	37.0	49.1	-12.1

The differences between calculated (from equation 4) and experimental values for depth of dehydrogenation for mixtures containing 30, 50, and 70 mol-% of toluene are 0.8-1.2, 1.0-1.8, and 3.5-4.1%, respectively. It has already been pointed out that the corresponding differences with nitrogen as diluent do not exceed 1.3%. Dilution with toluene (up to 70 mol-%) thus gives the same effect as with nitrogen. Toluene, in the same way as nitrogen, shifts the equilibrium point to the right, and adsorption of toluene at active centers of the catalyst does not significantly affect the depth of dehydrogenation of ethylbenzene.

When, however, the toluene concentration is raised to 85%, the difference between calculated and experimental values increases to 12%. This abrupt rise is ascribed to rapid inactivation of the active centers at high toluene concentrations. There are references in the literature [6] to rapid inactivation of the catalyst by toluene, and in particular by benzene (or, more probably, by the products of their transformation at the catalyst surface).

and these observations agree with ours. We found that when equal portions of ethylbenzene-toluene mixture (70% toluene) are passed over the catalyst, the depth of dehydrogenation of ethylbenzene rises with increasing molar velocity (Table 5).

TABLE 5

Dehydrogenation of 3:7 ethylbenzene-toluene mixtures

Expt. No.	Ml of mixture passed		Volume velocity of the mixture	Molar velocity of the mixture	Yield of catalyze as % of mixture introduced	Styrene content of catalyze, as % of wt.	Depth of dehydrogenation, %		Difference, %
	before the experiment	during the experiment					found	calcd. from equation (4)	
1	2	3	4	5	6	7	8	9	10
14	8	10	1.00	9.0	93	10.1	30.6	38.7	-8.1
12	8	10	1.55	14.0	95	10.9	33.0	38.7	-5.7
13	11	12	1.84	16.8	96	11.6	35.2	38.7	-3.5
15	14	16	2.40	21.7	96	11.4	34.6	38.7	-4.1

It is of interest that the depth of dehydrogenation of undiluted ethylbenzene remains constant over the same range of molar velocities (Fig. 3). This difference may be explained as being due to rapid inactivation of the catalyst

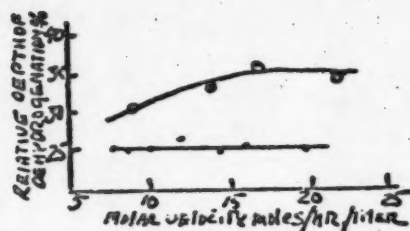


Fig. 3. Dehydrogenation of ethylbenzene without diluent, and diluted with toluene: ● - ethylbenzene without diluent; ○ - ethylbenzene-toluene mixture.

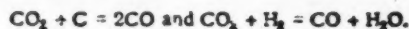
by the products of transformation of toluene; the faster the mixture passes over the catalyst, the less time is there for toluene or its transformation products to undergo adsorption at the active centers. Toluene thus influences the reaction in two ways: as an inert diluent it displaces equilibrium in the direction of styrene production, but by lowering the activity of the catalyst it reduces the velocity of the reaction. Hence the depth of dehydrogenation of ethylbenzene rises with increasing toluene content of the mixtures, but at the same time the difference between calculated and experimental values also rises.

Discussion of Results

The results of this research may be summarized as follows. The yields of styrene obtained by dehydrogenation of ethylbenzene without a diluent are constant over a wide

range of molar velocities. Dilution with hydrogen causes a sharp fall in the depth of dehydrogenation, the experimental values for which are only 3-4% higher than the calculated ones. The depth of dehydrogenation rises with increasing nitrogen content of the mixtures, and these values agree well with those derived from thermodynamic calculations; at equal dilutions the effects obtained with nitrogen or with toluene (up to 70%) are practically identical, showing that the reaction attains thermodynamic equilibrium, and hence that the effect of inert diluents is to shift the equilibrium point in the direction of styrene production.

However, not all the diluents usually considered as inert (CO_2 , H_2O) are in fact inert. Thus it is known that the effluent gases obtained during dehydrogenation of ethylbenzene diluted with CO_2 contain up to 50% of carbon monoxide [3], which may arise by one of the reactions:



Both reactions raise the dilution of the equilibrium mixture, owing to access of CO or H_2O , and thereby raise the yields of styrene. Apart from this, the oxidation of some of the hydrogen, and thus its removal from the reaction leads to a further displacement of the equilibrium. Tolstopiatova [4] found a greater depth of dehydrogenation of ethylbenzene with carbon dioxide at 575° than we did with nitrogen.

The opposite effect is obtained as a result of the reaction of steam with "coke": $\text{H}_2\text{O} + \text{C} = \text{CO} + \text{H}_2$; the hydrogen produced causes a fall in the yield of styrene. Our experiments showed that the yields of styrene were

2-2.5 times smaller when carbon dioxide in the mixtures was replaced by equal volumes of steam. Thus it appears that the yields of styrene obtained under the same conditions may vary according to the nature of the diluent, and the differences may be due to kinetic as well as to thermodynamic factors.

The results obtained afford further evidence that changes in the depth of reaction following dilution with inert substances or reaction products may be due not to differences in the adsorption constants but to the reaction attaining its equilibrium point. These results may serve for the critical revision of certain currently held views [1,3,4,5,6] on the role of inert diluents in the dehydrogenation of ethylbenzene.

SUMMARY

1. A study has been made of the reaction of catalytic dehydrogenation of undiluted ethylbenzene at 575°, and of its mixtures with hydrogen, nitrogen and toluene.

2. It is shown that the reaction attains a state of thermodynamic equilibrium over a wide range of flow velocities, and that the role of inert diluents depends on displacement of the equilibrium point.

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Institute of Organic Chemistry
Academy of Sciences USSR

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POISONING OF PLATINUM CATALYSTS WITH A LOW CONTENT OF ACTIVE METAL ON A CARRIER, UNDER CONDITIONS OF DEHYDROGENATION CATALYSIS

Kh. M. Minachev, N. I. Shulkin, and I. D. Rozhdestvenskaya

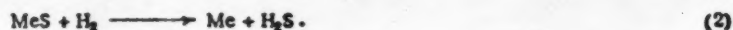
It has been firmly established that only very small amounts of poisons are required for the inactivation of catalysts, as is shown by a survey of the extensive literature of the subject [1,2,3].

According to N. D. Zelinsky [4] the cause of inactivation of metal-containing catalysts under conditions of hydrogenation or dehydrogenation catalysis, and in the absence of specific poisons, is the formation of the so-called "carbonaceous film" on the catalyst surface. This film arises by the partial decomposition of the substrates, and by occluding the active surface inhibits the catalytic reaction. Zelinsky showed that surfaces thus inactivated may be reactivated by the action of atmospheric oxygen [5].

Shulkin, Novikov, and Tulupova [6] found that rapid inactivation of a platinized charcoal dehydrogenation catalyst (5% Pt) took place with cyclopentadiene, 1-ethycyclopent-1-ene, and allylcyclopentane, but not with cyclohexene or alkenes. This effect was ascribed by the authors to partial dehydrogenation of five-membered cycles, to give labile dienes, the polymers of which occlude the active centers of the catalysts. In one of our earlier papers [7] we explained the fall in activity of platinum catalysts under conditions of occlusion of active centers by carboids as being due to the possibility of formation of qualitatively different active centers, able to promote fission of six-membered hydrocarbon rings, when large deformations of the crystal lattice exist. Freidlin and Ziminova [8] ascribe inactivation of catalysts to depromotion during the reaction.

Rubinshtein and Pribytkova [9], in studying the action of thiophen on Ni-Mg catalyst of dehydrogenation of cyclohexane or of hydrogenation of benzene, found that the more highly disperse catalysts are the more resistant to poisons. On the basis of changes in the energy of activation of the reaction of dehydrogenation of cyclohexane according to the amount of poison introduced, the authors draw certain conclusions regarding the mechanism of poisoning of catalysts (in the given case by chemisorption of the poison), and as to the heterogeneity of the catalyst surface.

We know from the work of Zelinsky et al. [10] that platinum catalysts used for aromatization of gasoline hydrocarbons are sensitive to the action of sulfur compounds contained therein. Thus Zelinsky and Shakhnazarova [11], in their study of poisoning of platinized charcoal by sulfur-containing compounds in cyclohexane at 300-350°, show that the dehydrogenating activity of the catalyst falls regularly, but its desulfurizing activity is retained. The catalyst is reactivated by passing pure cyclohexane; the hydrogen liberated combines with bound sulfur, removing it as hydrogen sulfide. Zelinsky [10] represents the processes of poisoning of catalyst by sulfur compounds, and of its regeneration, as follows:



Inactivation of the catalysts is, however, studied in the researches quoted above only qualitatively.

In planning this research on poisoning of platinum catalysts, consisting of small amounts of platinum on a carrier, we hoped to elucidate the following points:

- (1) to determine the stability of catalysts of dehydrogenation of cyclohexane, according to the amount of poison introduced, and to the platinum content of the catalysts;
- (2) to find the relationship between molecular structure of the poison and its inactivating power;
- (3) to find changes in the energy of activation of the reaction of dehydrogenation of cyclohexane and in the pre-exponential term of the Arrhenius equation before and after poisoning of the catalysts;
- (4) to find whether the poisons cause any structural change in the catalysts; and
- (5) to investigate the possibility of regenerating poisoned catalysts.

EXPERIMENTAL

Catalysts. The catalysts were prepared from activated charcoal, and contained 3.21, 1.41, 0.62 and 0.37% of platinum; only the concentration of chloroplatinous acid was varied, all other conditions being maintained uniform.

Poisons. The following catalyst poisons were used: n-propylmercaptan, isoamylmercaptan, thiophen, triophan, diethyl sulfide, diisoamyl sulfide, hydrogen sulfide, and carbon disulfide.

Cyclohexane. This had b.p. 80.6°/760 mm, d_4^{20} 0.7779 and n_D^{20} 1.4263.

Apparatus. All experiments were performed under strictly standardized conditions. The reaction tube, diameter 14 mm, was placed in an electric oven 90 cm in length. 2.5 g of catalyst was placed in a layer 5.5-6 cm long, in the middle of the tube. The temperature was measured by means of a thermocouple placed at the center of the layer of catalyst; the temperature did not usually vary more than $\pm 1^\circ$ during the experiments. Cyclohexane was delivered to the reaction zone at a uniform rate, by means of an automatic burette with a piston propelled at a uniform rate by a synchronous motor. The gas was measured by a buret: volume 1000 ml, graduated in 2 ml, with a constant level.

Experiments. The catalysts were reduced in a stream of electrolytic hydrogen at a temperature gradually rising to 310°, the process taking 4 hrs. Dehydrogenation of cyclohexane, with or without poisons, was conducted without addition of hydrogen. The effect of poisons was studied by passing 10 ml of cyclohexane containing 0.0005 g of organic sulfur, at 280°. The extent of conversion of cyclohexane into benzene was derived from refractive index measurements of the catalyzate and from measurement of the volume of hydrogen produced. After poisoning the catalysts (before determining their activity) the value of the activation energy of the reaction of dehydrogenation of pure cyclohexane (not containing poison) was determined, using poisoned catalyst. Activation energy was also determined for all catalysts before exposure to the poisons.

In the kinetic experiments, the levels of the piston and of the water in the gas pipet were read after the required temperature had been reached, and the experiment was begun. The gas was passed through for 10-15 min., during which time the temperature of the oven became constant. Measurements of the temperature, of the volume of gas produced, and of the amount of cyclohexane used were made every 5 min. The volume of hydrogen produced was reduced to NTP, taking into account the level of the water in the gasometer for each experiment. The length of the experiments varied from 45 to 100 min.

Kinetics of dehydrogenation of cyclohexane, using platinum catalysts with different contents of metal, before their poisoning.

In order to elucidate the mechanism of poisoning of the catalysts it was necessary to compare the kinetics of the reaction with catalysts before and after poisoning. It had been established in preliminary experiments that the activity of the catalysts remains constant for a long time when used with pure cyclohexane. The gas evolved consisted of hydrogen with 1.5% of saturated hydrocarbons, apparently cyclohexane carried over by the strong stream of hydrogen. These results showed that we could take the volume of hydrogen produced in unit time as a measure of the velocity of dehydrogenation of cyclohexane. The rate of delivery of cyclohexane was in all cases 0.5 ml in 5 min. (volume velocity 0.05 liters per liter of catalyst per hr).

The results obtained are given in Table 1, and Fig. 1 represents the temperature dependence of velocity of reaction. The points obtained all lie on straight lines, showing that the reaction follows the Arrhenius equation. As appears from Table 1, catalysts containing 3.21 and 1.41% of Pt gave results (Q and K_0) differing by amounts close to the experimental error of the determinations. As the Pt content of the catalysts diminishes, the number of active centers rises relatively, being several times as great, for example, for catalyst No. 2 (1.41% Pt). These active centers are evidently of lower activity, since increase in the number of active centers is associated with an increase in activation energy of up to 3300 cal/mol, this result being considerably beyond the limits of experimental error.

Poisoning of catalysts

The time when hydrogen sulfide began to appear in the issuing gases was found by means of preliminary experiments. Qualitative reactions for thiophen in the catalyzate were negative, showing that the whole of the sulfur introduced was held on the catalysts. The tables and curves are based only on data obtained before appearance of hydrogen in the effluent gases, i.e., while the whole of the sulfur was still bound on the catalysts.

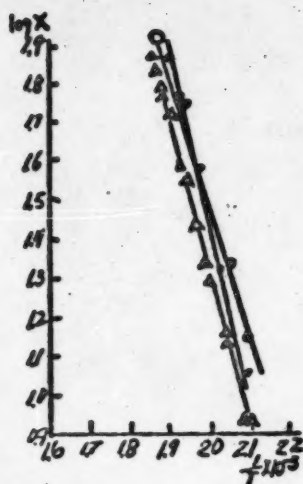


Fig. 1. Dependence of velocity of reaction on temperature, with the catalysts: o - 3.21% Pt on charcoal; ● - 1.41% Pt on charcoal; Δ - 0.62% Pt on charcoal; ▲ = 0.37% Pt on charcoal.

Tables 2 and 3 show % dehydrogenation of cyclohexane according to the amount of sulfur introduced, and to the nature of the sulfur-containing compound, and Fig. 2 gives typical poisoning curves. The introduction of 1-3 portions of poison has practically no effect on the activity of catalyst No. 1 (3.21% Pt). Successive further portions each lower the activity by 6-10%, but the activity is still considerable even after 11 portions. The general process of poisoning of the catalysts is much the same for all the sulfur-containing compounds, except for catalyst No. 1, which is inactivated more rapidly by one group of poisons (propyl mercaptan, isoamyl mercaptan, thiophen) than by another (diethyl and diisoamyl sulfide, thiophan, hydrogen sulfide).

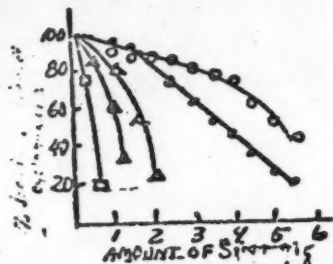


Fig. 2. Dependence of % dehydrogenation of cyclohexane on the amount of sulfur introduced: c - diisoamyl sulfide, catalyst No. 1 (3.21% Pt on charcoal); ● - n-propyl mercaptan, same catalyst; Δ - thiophen, catalyst No. 2 (1.41% Pt on charcoal); ▲ - n-propyl mercaptan, catalyst No. 3 (0.62% Pt on charcoal); □ - n-propyl mercaptan, catalyst No. 4 (0.37% Pt on charcoal).

It was of interest to compare these results with those obtained with catalysts poisoned with hydrogen sulfide. Catalysts No. 1 (3.21% Pt) and No. 2 (1.41% Pt) were poisoned with hydrogen sulfide, mixtures of which with hydrogen were passed together with cyclohexane through the catalysts. Passage of 3.8 ml of hydrogen sulfide (containing 0.0054 g of sulfur) through catalyst No. 1 reduced dehydrogenation of cyclohexane from 99.8%

TABLE 1

Kinetic data for dehydrogenation of cyclohexane in presence of platinumized charcoal catalysts containing different amounts of platinum

Platinum content of catalyst, %	Expt. No.	T	v_0 for 10 min.	$\frac{1}{x}$ conversion, %	Q	K_0
1	2	3	4	5	6	7
3.21	29	473	80.6	13.8	14780	$3.38 \cdot 10^3$
	30	489	136.0	21.8		
	31	527	535.0	85.8		
	32	519	364.0	58.4		
1.41	77	515	348.8	56.0	15250	$1.66 \cdot 10^3$
	76	488	135.0	21.6		
	79	473	74.0	11.8		
	80	503	239.0	38.0		
	81	526	468.0	75.2		
	59	536	432.0	69.4		
0.62	60	526	330.0	53.0	17360	$8.52 \cdot 10^3$
	61	475	54.0	8.6		
	62	488	92.0	14.6		
	63	507	172.0	27.6		
	64	499	126.0	20.0		
	65	512	226.0	36.0		
	66	531	388.0	62.2		
0.37	88	539	481.2	77.2	18080	$1.07 \cdot 10^3$
	89	528	383.0	61.4		
	100	516	245.0	39.2		
	101	503	141.0	22.4		
	102	479	57.0	9.0		
	103	491	87.0	13.8		

(n_D^{20} of catalyzate 1.5000) to 27.8% (n_D^{20} of catalyzate 1.4413). Passage over catalyst No. 2 of 1.46 ml of hydrogen sulfide (0.0021 g of sulfur) reduces depth of dehydrogenation from 97.6% (n_D^{20} of catalyzate 1.4980) to 14.3% (n_D^{20} of catalyzate 1.4340). A comparison of the results obtained with hydrogen sulfide with those given by other sulfur-containing poisons showed that they all give approximately the same degree of inactivation of the catalysts per unit weight of sulfur, irrespective of the structure of the poison. It follows either that the mean life of the different molecules of poisons at the catalyst surfaces is the same, or that the catalysts decompose the various poisons with production of hydrogen sulfide at about the same rates, in which case the poison is actually hydrogen sulfide in all cases.

TABLE 2

Dependence of % dehydrogenation of cyclohexane on the amount of sulfur introduced into catalyst No. 1 (3.21% Pt)*

Expt. No.	Sulfur compound Amount of sulfur introduced in g	% Dehydrogenation of cyclohexane						
		propyl mercaptan	isoamyl mercaptan	thiophen	diethyl sulfide	disoamyl sulfide	thiophan	hydrogen sulfide
1	0.0005	98.6	98.0	97.6	96.0	95.0	93.8	98.6
2	0.0010	96.4	98.0	95.2	93.0	88.6	89.2	93.6
3	0.0015	96.8	96.0	96.6	89.2	86.2	88.6	92.3
4	0.0020	86.8	89.6	92.6	88.0	86.0	85.8	86.0
5	0.0025	72.4	74.3	87.0	87.7	83.0	82.4	82.4
6	0.0030	63.0	66.4	73.0	83.0	79.0	80.0	78.4
7	0.0035	53.6	63.0	62.4	76.6	76.6	77.0	73.0
8	0.0040	47.5	51.0	50.8	72.0	73.0	74.0	64.6
9	0.0045	37.8	42.3	39.4	64.6	62.0	58.8	53.0
10	0.0050	27.0	32.8	29.8	53.0	51.3	50.4	46.0
11	0.0055	19.4	25.8	20.0	36.0	40.3	40.8	30.0

* Volume of catalyst 10 ml, weight 2.5 g, containing 0.0830 g of platinum, volume velocity of reaction mixture 0.65.

Calculations based on our experimental data show that the amount of sulfur which had to be added in order to lower the activity by 70-80% amounted to 5-7% of the weight of active metal contained in the catalyst, corresponding with 3 atoms of platinum per atom of sulfur.

Dependence of poisoning of catalysts on nature of carrier.

The results described above show that the amount of sulfur required to poison platinum catalysts with charcoal carrier is quite considerable in relation to the content of highly dispersed platinum. It was hence thought that the nature of the carrier may play a significant role in the process of inactivation of the catalysts. This possibility was checked on two catalysts, in which the carrier was silica gel or ultra-porous glass. These catalysts were much more rapidly inactivated by sulfur compounds than were those with charcoal carriers. The stability of the catalysts fell in the series charcoal, silica gel, porous glass carrier.

Poisoning of catalyst No. 5 (1% Pt on silica gel) was studied under the same conditions as for platinized charcoal catalysts, using thiophen as the poison; 7.75 g of catalyst, containing 0.0775 g of platinum, were taken, and the results are given in Fig. 3.

As is evident from Fig. 3 only 0.0022 g of sulfur is required to inactivate this catalyst, as compared with 0.0055 g, or nearly 2.5 times as much for a charcoal catalyst of about the same platinum content.

Kinetic data for dehydrogenation of cyclohexane before and after poisoning of platinized silica gel catalyst are given in Table 4, and Fig. 4 gives the velocity-temperature curves. A comparison of the values of Q and K_p before and after poisoning shows that the fall in activity of the catalyst is in this case also due exclusively to the

reduction in the number of active centers (cf. kinetic data for dehydrogenation in presence of platinized charcoal); the energy of activation remains the same after poisoning, while K_a falls noticeably.

TABLE 3

Dependence of % dehydrogenation of cyclohexane on the amount of sulfur introduced into the catalysts*

Catalyst	Sulfur Compound	% Dehydrogenation of cyclohexane						
		propyl mercaptan	isoamyl mercaptan	thiophen	diethyl sulfide	diisoamyl sulfide	thiophan	hydrogen sulfide
No.2 (1.41% Pt) containing 0.0353 g of platinum	0.0005	98.0	92.6	92.8	90.0	93.4	95.0	92.4
	0.0010	86.0	85.0	81.0	86.6	87.0	78.0	85.0
	0.0015	56.0	55.8	54.8	55.0	56.0	51.0	65.0
	0.0020	30.0	28.0	25.0	19.4	18.8	21.5	44.6
	0.0025	—	—	—	—	—	—	20.1
No.3 (0.62% Pt) containing 0.0155 g of platinum	0.00025	83.6	85.9	—	—	86.0	84.0	—
	0.00050	62.0	63.4	—	—	61.8	65.2	—
	0.00075	35.6	30.5	—	—	34.8	38.5	—
No.4 (0.37% Pt) containing 0.0093 g of platinum	0.00025	73.4	—	72.8	—	71.5	75.2	—
	0.00065	21.7	—	16.8	—	19.4	20.4	—

* Volume of catalyst 10 ml, weight 2.5 g, volume velocity of reaction mixture 0.65.

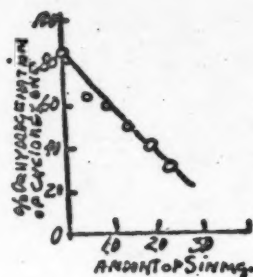


Fig. 3. Dependence of depth of dehydrogenation of cyclohexane on the amount of sulfur introduced. Catalyst No. 5 (1% Pt on silica gel):

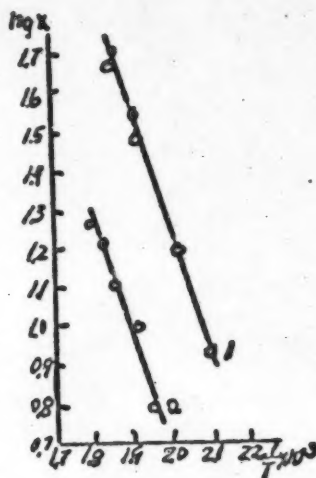


Fig. 4. Relation between velocity of dehydrogenation of cyclohexane and temperature, on catalyst No. 5 (1% Pt on silica gel): 1) before poisoning; 2) after poisoning.

Poisoning of catalyst No. 6 (1.08% Pt on porous glass). The catalyst was poisoned with thiophen under the same conditions as for the preceding catalysts, 13 g of catalyst containing 0.1404 g of platinum being placed in the reaction tube. The results are represented in Fig. 5, from which it appears that poisoning of this catalyst requires

only 0.0020 g of sulfur, i.e. 2.75 times less than for catalyst No. 1, although catalyst No. 6 contains 1.75 times more platinum.

TABLE 4

Kinetic data for dehydrogenation of cyclohexane in presence of platinized silica gel.

Expt. No.	T	v_0 for 10 min.	x dehydrogenation, %	Q	K_0
Before poisoning					
1	537	344.0	52.0	14600	$4.909 \cdot 10^7$
2	521	233.0	35.4		
3	494	103.8	16.0		
4	478	56.4	8.6		
5	521	200.1	31.0		
6	538	318.0	48.5		
After poisoning					
16	555	121	18.6	14650	$1.253 \cdot 10^7$
17	538	83	13.0		
18	525	65	10.0		
19	510	40	6.0		
20	547	110	16.5		

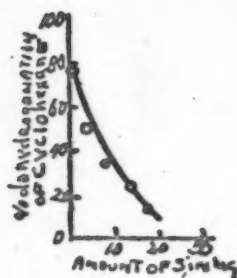


Fig. 5. Dependence of depth of dehydrogenation of cyclohexane on the amount of sulfur introduced. Catalyst No. 6 (1.09% Pt on glass).

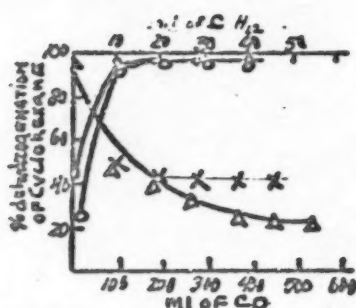


Fig. 6. Poisoning and regeneration of a catalyst containing 1.41% Pt on charcoal: X - poisoning with CO at 300°; Δ - poisoning with CO at 280°; ● - regeneration of catalyst poisoned at 300°; ○ - regeneration of catalyst poisoned at 280°.

of hydrogen evolved increases linearly with time. These preliminary experiments permitted the study of the kinetics of dehydrogenation of cyclohexane with Catalyst No. 1 (3.21% Pt-C) after poisoning with three poisons, with Catalyst No. 2 (1.41% Pt-C) poisoned with two poisons, and with Catalyst No. 3 (0.62% Pt-C) poisoned with one poison.

The experimental results so obtained are given in Table 5 and in Figure 9, which shows dependence of velocity of reaction on temperature. The points are all on straight lines, showing that the reaction follows the Arrhenius equation. A comparison of the values of activation energy for the catalysts before poisoning (Table 1, column 6) and after poisoning (Table 5, column 6) shows that they remain practically unaltered. Thus changes in the activity of the catalysts must be due only to change in the number of active centers, as is shown by the constancy of the

The experiments show that the nature of the carrier profoundly affects the sensitivity of the catalysts to the action of poisons. The relatively high stability of platinized charcoal, as compared with platinized silica gel or glass, is connected with both the nature of the carrier and with its specific surface.

Poisoning of catalyst No. 2 (1.41% Pt) with carbon monoxide. The effect of carbon monoxide on platinized charcoal under conditions of dehydrogenation catalysis has not yet been studied. We conducted our experiments at 280 and 300°. The rate of delivery of cyclohexane and the amount of catalyst taken were the same as for the experiments on poisoning with sulfur-containing substances. In each experiment 10 ml of cyclohexane and 100 ml of carbon monoxide were passed over the catalyst. The results obtained are represented in Figure 6, from the curves of which it appears that at 280° the activity of the catalyst falls to less than half after passing 91.4 ml of carbon monoxide, and then falls by another 10-12%, after which it remains constant.

A somewhat different picture is given by experiments at 300°: the first portions of poison lower activity to about the same extent as at 280°, but further portions of carbon monoxide caused no more lowering of activity. Catalyst poisoned with carbon monoxide very quickly regains its former activity; thus the activity of the catalyst is fully restored by passing 20 ml of cyclohexane, after poisoning at 280 and 300°. It follows that carbon monoxide exerts only a transient action.

Study of the Kinetics of Dehydrogenation of Cyclohexane With Poisoned Catalysts

Preliminary experiments showed that when cyclohexane is passed over poisoned catalysts at temperatures equal to or lower than that at which poisoning took place the activity of the catalyst remains practically unaltered. The results obtained are given in Figures 7 and 8, which show that the volume

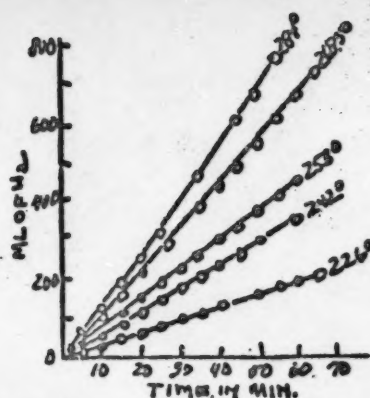


Fig. 7. Dependence of volume of hydrogen evolved on time; catalyst (3.21% Pt-C) after poisoning with thiophen.

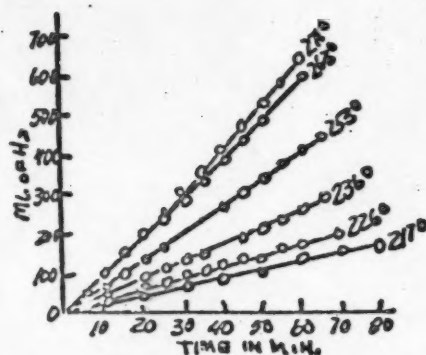


Fig. 8. Dependence of volume of hydrogen evolved on time; catalyst (1.41% Pt-C) after poisoning with n-propyl mercaptan.

catalysts is not changed by poisoning, and that they contain only one crystalline phase - platinum. The results are given in Table 6.

The platinum crystal lattice for catalysts containing less than 1% of platinum was an expanded one; this is characteristic of catalysts containing solid solutions of hydrogen, which would be formed in the special conditions of our experiments. A comparison of the lattice constants before and after poisoning shows clearly (in accordance with the absence of additional lines on the roentgenograms) that poisoning is not due to formation of compounds or solid solutions of the poison with platinum. The results of the X-ray studies agree well with the earlier described experiments establishing the constancy of Q and the variability of K_0 in the Arrhenius equation.

It follows that both structural and kinetic data indicate that the mechanism of poisoning is one of blocking of active centers, but not of chemisorption.

Regeneration of Poisoned Catalysts

The regeneration of poisoned catalysts is a very important problem in heterogeneous catalysis practice.

* We wish to express our gratitude to Doctor of Chemical Sciences A. M. Rubinshtein, who conducted the roentgenographic study of the catalysts.

activation energy and by the change in the value of K_0 in Arrhenius' equation. Comparison of the values of K_0 for catalysts before poisoning (Table 1, column 7) and after poisoning (Table 5, column 7) shows that K_0 for poisoned catalysts is 2.3 to 22.4 times smaller than their initial values, while the activation energies remain practically constant.

It follows from the results presented that our catalysts are highly homogeneous with respect to their properties.

X-Ray Data for the Catalysts Studied*

The structure of the catalysts used in this research was studied roentgenographically, before and after they had been poisoned with various sulfur-containing substances. The roentgenograms show that the phase composition of the

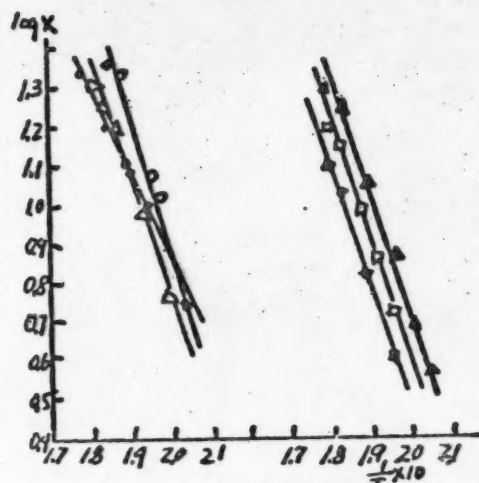


Fig. 9. Dependence of the velocity of dehydrogenation of cyclohexane on temperature, using catalysts poisoned with various substances: O - propyl mercaptan (catalyst No. 1; 3.21% Pt-C); ● - thiophen (same catalyst); △ - diethyl sulfide (same catalyst); ▲ - propyl mercaptan (catalyst No. 2; 1.41% Pt-C); - thiophen (same catalyst); ▤ - propyl mercaptan (catalyst No. 3; 0.65% Pt-C).

TABLE 5

Kinetic data for dehydrogenation of cyclohexane in presence of platinumized charcoal catalysts poisoned with sulfur containing substances

% Pt in catalysts	No. of experiments	T	v_0 for 10 min.	α , % dehydrogenation	Q	K_0	Catalyst poison
1	2	3	4	5	6	7	8
3.21	50	513	72.0	11.7	16046	$7.81 \cdot 10^7$	Propyl mercaptan
	51	507	64.6	10.5			
	52	491	33.4	5.5			
	53	529	135.0	22.0			
	54						
3.21	262	554	136.6	22.0	15220	$4.57 \cdot 10^7$	Thiophan
	263	541	112.0	18.0			
	264	526	76.0	12.0			
	265	515	60.0	9.9			
	266	526	81.0	13.0			
3.21	384	553	125.0	20.6	15080	$2.29 \cdot 10^7$	Diethyl sulfide
	383	543	113.0	18.0			
	384	535	97.8	16.0			
	356	530	89.0	15.0			
	387	515	59.0	9.5			
1.41	388	500	30.0	6.0	15360	$2.51 \cdot 10^7$	Propyl mercaptan
	91	557	120.4	19.5			
	92	545	107.6	17.6			
	93	536	98.2	16.0			
	94	526	68.8	11.3			
1.41	95	509	44.6	7.3	16000	$3.74 \cdot 10^7$	Thiophan
	96	490	22.4	3.6			
	97	499	29.6	5.0			
	282	557	96.0	15.7			
	283	547	94.0	15.0			
0.62	284	531	59.0	9.6	16360	$3.82 \cdot 10^7$	Propyl mercaptan
	285	520	42.2	7.0			
	286	510	32.4	5.3			
	70	555	77.4	12.7			
	71	529.3	40.2	6.6			
0.62	72	512	24.8	4.0			
	73	545	67.0	10.9			

The effect of all the poisons is equal to that of an equivalent amount of hydrogen sulfide.

2. The structure of the poison molecule does not affect its action, suggesting that they are all decomposed at the catalyst surface at about the same rate, with production of hydrogen sulfide.

3. The amount of organically combined sulfur required to poison the catalysts is proportional to the amount of platinum contained therein.

4. The amount of sulfur required to lower the activity of catalysts by 70-80% is about 6-7% of the weight of platinum present on the carrier.

TABLE 6

Changes in the crystal lattice constants of platinum in different samples of catalysts before and after poisoning

% Pt in catalysts	α_{Pt} before poisoning, in Å	α_{Pt} after poisoning, in Å
0.37	4.09	4.020
0.62	3.998	3.914
1.41	3.910	3.890
3.21	3.880	3.850

Experiments were done on regeneration by means of cyclohexane of three platinum catalysts on different carriers poisoned with thiophen. Cyclohexane was passed at a volume velocity of 0.65 l per l of catalyst per hr. at 300°, in 10 ml portions. The results, presented in Fig. 10, show that platinumized charcoal very quickly regains its initial activity, after passage of 70 ml of cyclohexane.

Platinumized silica gel also regains its activity, although the initial value is not restored; activity cannot be raised to the initial value of 84% dehydrogenation. Practically no regeneration of platinum on porous glass takes place. This difference in the behavior of platinum catalysts on different carriers after poisoning with the same substance is of considerable interest; the reason for the differences is not clear, and further studies are required.

SUMMARY

1. Poisoning by means of sulfur containing compounds of dehydrogenating catalysts consisting of different concentrations of platinum on various carriers has been studied.

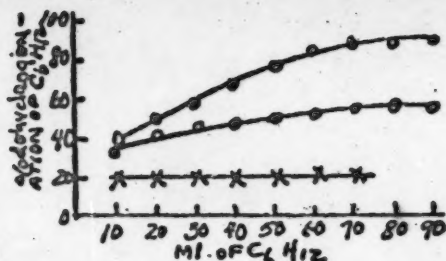


Fig. 10. Regeneration by means of cyclohexane of catalysts poisoned with thiophene: o - catalyst 1.41% Pt-C; middle curve - catalyst 1.0% Pt on silica gel; x - catalyst 1.08% Pt on glass.

5. The regenerability of platinum catalysts poisoned with one and the same substance varies according to the nature of the carrier.

6. It has been shown experimentally that the activation energy of the reaction of dehydrogenation of cyclohexane is the same for poisoned and unpoisoned catalysts. The value of the pre-exponential term of the Arrhenius equation is ten times smaller for poisoned than for fresh catalysts. These data, together with crystal lattice data, indicate that poisoning of platinum catalysts is due to occlusion of active centers.

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Institute of Organic
Chemistry
Academy of Sciences
USSR

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ELUCIDATION OF THE ROLE OF VARIOUS ADSORPTIONAL CENTERS IN THE REACTION OF HYDROGENATION OF ACETYLENE ON METALLIC NICKEL

STUDY OF THE ACTIVE SURFACE OF NICKEL BY MEANS OF A DIFFERENTIAL ISOTOPE METHOD

N. P. Keler

The differential isotope method of Keler and Roginsky [1-4] gives unambiguous evidence of the reality of the existence of inhomogeneities of active centers of adsorption, from activation energies and heats of adsorption for a number of typical catalysts and adsorbents. This allowed us to make a definite choice between "repulsion and inhomogeneity" when considering kinetic and equilibrium isotherms different from those found for uniform surfaces.

The experimental proof of the existence of inhomogeneity of active surfaces was of fundamental importance for the theory of adsorption and catalysis. For contact catalysts with proven heterogeneous surfaces, however, there still remained to be solved an even more difficult, but not less fundamental, problem, viz., to determine to what extent adsorptional centers with different heats of adsorption and with different activation energies actually take part in the catalytic process. In spite of the basic importance of the solution of this problem for the clarification of the intimate mechanism of catalysis, and for the elaboration of a theory of the velocity of catalytic processes, it has remained unsolved, owing to the lack of a direct method for its study. The differential isotope method, in combination with a study of the statistics of the active centers and of the kinetics of the reactions, now affords us all the necessary means for the solution of the problem.

The present paper presents the results of a study of the role of different active centers for adsorption of acetylene on metallic nickel, in the reactions of catalytic hydrogenation and methane formation.

EXPERIMENTAL

The method depended on the study of processes taking place in the adsorption layer when two successive portions of gas were passed, of which one contained a labelled stable or unstable isotope. If the reaction is of the type $2ABC \longrightarrow AB + C + A + BC$, adsorption is followed by desorption with small portions of gas. The isotope content of each component of the desorbed gas is then determined, and from this can be deduced from which adsorbed part of the gas the given component was formed. These experiments give a qualitative indication of the active centers at which the reaction takes place, and in which direction it goes. In the study of reactions of the type $A + B \longrightarrow AB$ adsorption of one of the components takes place in two portions, of which one contains labelled atoms. The catalyst is then treated with small portions of the second component, as a result of reaction with which the reaction products are evolved in the gaseous phase. Their isotope content is then determined, and from this it is concluded with which portion of adsorbed gas the second component had reacted. Knowing the dependence of the change in activation energy of adsorption on degree of filling of active centers it is possible to deduce at which centers of adsorption the catalytic reaction had taken place. The change in activation energy according to degree of saturation is derived from adsorption measurements.

1. Experimental methods

The nickel used was prepared by the method of Bag and Egupov, depending on extraction with alkali of a 1:1 nickel-aluminum alloy.* The given catalyst had a surface of 15 ± 1 sq.m. per g. as estimated from the adsorption isotherm for benzene. Before each experiment, the weighed portion of catalyst was degassed at 300° and reduced with hydrogen at the same temperature (the catalyst surface underwent partial oxidation even when it was stored under water), and was finally exhaustively degassed at $500^\circ/10^{-6}$ mm.

Ordinary acetylene was prepared from chemically pure calcium carbide, and was purified by repeated

* The author takes the opportunity of thanking G. V. Isagulyants for providing him with the catalyst.

fractionation in a vacuum apparatus. Acetylene labelled with C^{14} was prepared from labelled barium carbide, obtained from labelled barium carbonate by heating with magnesium by Maquenne's method [5]. We determined a temperature regime for this reaction, which ensured a 75-85% yield of acetylene, calculated on the carbon taken. Ordinary ethylene was prepared by dehydration of ethanol over a catalyst. Hydrogen and oxygen were prepared electrolytically, and were freed of traces of oxygen or hydrogen, respectively, by their combustion on palladized silica gel.

The C^{14} content was derived from measurement of the radiation of barium carbonate, by means of a counter with a mica window, thickness 4 mg/sq.cm. The specimens under measurement were placed on filter paper discs 2 cm in diameter, and the radiation was compared with that of standard specimens obtained under identical conditions from the original labelled acetylene. It was necessary, owing to the softness of the C^{14} radiation, to introduce a correction for its absorption by the emitting sample itself; this was effected by means of a calibration curve connecting specific activity of specimens of barium carbonate prepared from labelled acetylene with weight of precipitate. The C^{14} content of any carbonaceous gas was determined by burning it at an electrically heated platinum wire, and absorbing the carbon dioxide so produced in aqueous barium hydroxide, which was then filtered, to collect barium carbonate.

The apparatus used is shown in Fig. 1. The part B beyond the cocks 14 and 13 served for burning the gas under analysis and for absorbing the resulting carbon dioxide. Before introducing the gas, this part of the apparatus, with the absorption tube 6 attached, as shown in Fig. 1, was exhausted to a vacuum of 10^{-5} mm, and the gas was transferred from the reaction vessel 1 into the combustion vessel with the aid of a special diffusional mercury-condensational pump 5. The oxygen needed for combustion was taken from flask 7, at a pressure controlled by the manometer 8, in amount in excess of that required. The carbon dioxide formed was frozen out of the combustion gases, in a side-tube of the combustion vessel, and was then transferred to the trap 9, from which it was removed by means of a stream of CO_2 -free nitrogen, which swept it into the absorbent tube 6, the construction of which is clear from Fig. 1.

The cocks 10 and 11 were closed when all the carbon dioxide had been swept out, and the baryta water was slowly passed through the filter, to collect barium carbonate. The filter paper with precipitate was dried to constant weight before measurement of its β -radiation. The overall error in determining specific β -activity was taken as being identical with the error involved in determining the weight of the precipitate, since the error incurred in measuring β -activity by means of a counter may be made vanishingly small, by prolonging the time of counting. The accuracy thus varied according to the amount of precipitate formed, the error amounting to $\pm 20\%$ or more for precipitates weighing 0.5 mg or less, $\pm 10\%$ for 1 mg, and $\pm 2\%$ for 5 mg.

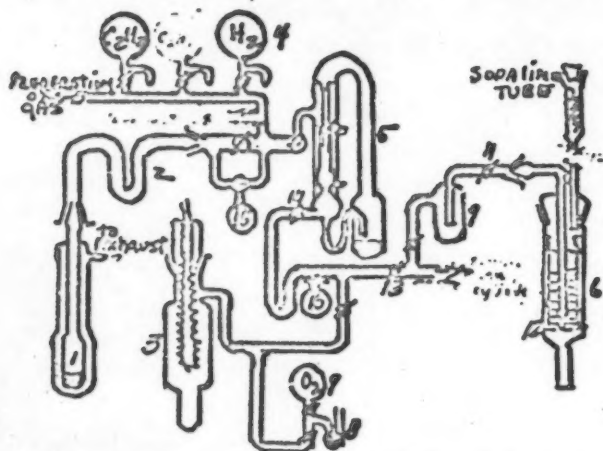


Fig. 1. Sketch of apparatus: 1) reaction vessel; 2) trap; 3) vessel for combustion of gases under analysis; 4) flasks for storage of gases; 5) mercury diffusional pump; 6) absorber; 7) flask; 8) manometer; 9) trap; 10-14) cocks; 15-16) McLeod manometers.

* The inaccuracy in the determination of the weight of the precipitates is connected with their variable water content, resulting from their hygroscopicity, and amounting to 0.5-0.1 mg.

Analysis of gas. The acetylene content of its mixtures with ethylene and ethane was determined by its adsorption on nickelous oxide, prepared by the thermal decomposition of thoroughly washed nickel carbonate. Adsorption proceeded with great rapidity, at a velocity many times greater than that of ethylene, which could be totally eliminated by heating the oxide in vacuum at 400° for 3-4 hrs. The partial pressure of acetylene did not exceed 10^{-4} mm after the separation. Ethylene was quantitatively separated from ethane by absorption in a solution of $HgSO_4$ in sulfuric acid.

2. Study of active surface by means of the differential isotope method

In distinction to ethylene, which was not adsorbed in appreciable amount by our catalyst, acetylene was actively adsorbed, in appreciable amount, at room temperature and below. Adsorption of acetylene was studied in static conditions in a vacuum apparatus, applying a previously described procedure [6-7], without any modification. Our first experiments showed us that only a part of the acetylene is adsorbed reversibly; the amount irreversibly adsorbed varies according to the activity of the given catalyst. Up to 40% of the surface of a specimen of nickel placed in the reactor in a damp condition bound acetylene irreversibly, as compared with only about 10% when the catalyst was first dried in a current of nitrogen; total adsorption in the latter case was also much smaller. The surfaces of the two specimens were approximately equal, as determined from the equilibrium isotherms for adsorption of benzene.

Desorption at over 150° of acetylene adsorbed at room temperature leads to evolution of methane and hydrogen, together with acetylene, although evolution of hydrogen was not observed during the adsorption process. At 500° it was found that 30% of adsorbed ethylene was recovered unchanged, and of the remaining 70% about 14% was accounted for by production of methane. The remaining acetylene underwent decomposition with production of hydrogen.

Experiments involving the application of the differential isotope method were applied to investigation of the uniformity of the active centers. Two portions of acetylene were adsorbed successively on a weighed amount of catalyst. The first portion consisted of ordinary acetylene, using 1.267 ml per g, and the second was labelled acetylene, (0.148 ml per g), being 90% and 10% of the total amount adsorbed, respectively. After completion of adsorption the reaction vessel was exhausted to a vacuum of 10^{-4} mm, for 2 min., after which desorption was effected by raising the temperature, simultaneously evacuating the desorbed gas from the reaction vessel to the space B by means of pump 5 (Fig. 1), which maintains a vacuum of 10^{-4} mm over the catalyst. In the portion of acetylene desorbed at up to 55°, representing less than 3% of the amount adsorbed, specific activity was only $3 \pm 0.5\%$ of that of the original labelled acetylene, adsorbed in the second portion. It may be concluded that the desorbed gas originates, to about 97%, from the first portion of gas adsorbed. The further portions of desorbate, containing methane and hydrogen, were not analyzed.

It follows from the results of this experiment that the surface is not uniform; if it had been, the probability of desorption of any molecule originating from the first or second portions of gas would have been equal, and the desorbed gases should have contained about 10% of labelled carbon compounds, whereas in fact they contained only 3%. It follows that there is no simple relationship between the activation energies of adsorption and desorption. This conclusion was confirmed by further experiments with labelled acetylene.

In these experiments, two, and in some cases three, portions of labelled and ordinary acetylene were passed over the prepared catalyst surface, in different orders. The first portion was usually totally adsorbed, while the second was adsorbed more slowly; the process was in many cases interrupted by pumping off the residual gas.

The first portion of hydrogenation products was removed from the surface at room temperature, by placing the catalyst with adsorbed acetylene in contrast with hydrogen. As a result, ethane and ethylene are formed, the former not being adsorbed on the catalyst, and the latter only very slightly. A considerable part of the hydrogen taken undergoes adsorption, without being used for hydrogenation.

The reaction gas thus obtained, under conditions of excess of hydrogen, consists chiefly (85-90%) of ethane. It was noticed that the ethylene content of the first portion of desorbed gas was lower than in subsequent ones. The whole of the adsorbed acetylene which is capable of hydrogenation does so at room temperature. Ethane and ethylene were usually absent from the gas obtained by treatment with hydrogen at higher temperatures, up to 200°; it contained methane, together with some acetylene which did not under these conditions undergo hydrogenation. In order to be sure that hydrogenation takes place at those active centers at which adsorption had taken place, but that it does not take place at some other kind of active center, to which the acetylene found in the desorption gas had been bound, a number of experiments were performed, in which prolonged desorption was carried out at room temperature, before admission of hydrogen, freezing out the acetylene in a special trap.

All the gaseous products obtained by the above methods from the catalysts were analyzed for their C^{14} content; ethane and ethylene were analyzed together. Knowing the C^{14} content it is possible to estimate how much each succeeding portion of acetylene had contributed towards the formation of the given reaction product. Analysis showed that with low degrees of saturation of the surface, up to 30%, there is no exchange of acetylene molecules adsorbed from the first portion of gas with those of the unadsorbed part of the second portion, although this does take place to a small extent (up to 5%) with higher saturations. The experimental results are presented

In Table 1; the catalyst was metallic nickel introduced wet into the reaction vessel.*

The first experiments showed that not all centers of adsorption are catalytically active for the hydrogenation reaction. If the probability of reaction of all adsorbed molecules were the same, we should expect the C^{14} content of any of the portions of ethane obtained to be equal to the mean value for adsorbed acetylene; we found that this was never the case. Thus in Experiment 12 two portions of acetylene were adsorbed on 0.65 g of catalyst. The first portion consisted of 2.81 ml of ordinary acetylene, sufficient to cover 46% of the catalyst surface (the area occupied by 1 molecule of acetylene was taken as $6 \cdot 10^{-16}$ sq. cm.), and the second was 1.23 ml of labelled acetylene, covering 20% of the surface; the average content of labelled acetylene in adsorption was 30%.

In this experiment, the pressure over the catalyst was lowered to 10^{-4} mm for 1 min. before admitting hydrogen. Ethane and acetylene in the issuing gases were separated out by freezing in liquid nitrogen. The ethane was separated, and transferred to the combustion vessel, and its C^{14} content was determined; it was found to be 57.2% of its amount in the initial portion of labelled acetylene. Hence this portion of ethane contained 43% of hydrogenated acetylene molecules from the ordinary acetylene adsorbed from the first portion, and 57% from the second. Altogether, 4.0% of the adsorbed acetylene underwent hydrogenation in this portion.

A second portion of hydrogen left in contact with the catalyst for a long time at room temperature hydrogenated only 0.8% of the adsorbed acetylene, the gas evolved not being analyzed. A third portion was obtained by heating at up to 150° in presence of hydrogen, and in these conditions acetylene was desorbed; almost all of this (94.1%) was derived from the second, labelled portion of acetylene. With further rise in temperature, in absence of hydrogen, a gas not containing components condensing at -182° was obtained, and this gas was shown to consist of methane and hydrogen. It contains mainly methane at $150-200^\circ$, but the hydrogen content rises with increasing temperature above this. The virtual absence of C^{14} ($3 \pm 0.3\%$) from methane desorbed at 400° testifies to its origin from the first portion of adsorbed acetylene.

This experiment thus suggests the presence of three groups of active centers: (1) active centers at which reversible adsorption of acetylene takes place, but not its hydrogenation, (2) active centers of adsorption at which hydrogenation takes place, and (3) active centers of adsorption at which formation of methane and hydrogen takes place.

It was thought to be of interest to find the energy of activation of adsorption at the centers where methane is formed. With this object, in experiment 13 three successive portions of acetylene were adsorbed, instead of the usual two; the first consisted of 0.328 ml of labelled acetylene (about 16% of the total amount adsorbed), the second of 1.142 ml (54.6% of total adsorbed) of ordinary acetylene, and the third of 0.619 ml (about 30% of total adsorbed) of labelled acetylene. In this experiment the first portion of gas was subjected to desorption for 170 min. at room temperature, during which time only 4% of the amount adsorbed had been removed; the corresponding figures for the second and third portions were 2.4% and 1.6%. Desorption was then continued for a further 15 hrs. at room temperature, but the amount of gas so collected was insufficient for analysis. The next portions of gas were removed by hydrogenation at room temperature; about 2.5% of the adsorbed acetylene underwent hydrogenation during 263 min. The ethane (containing traces of ethylene) so formed was derived (66%) from the second and (34%) third portions of acetylene.

As in the previous experiments, raising the temperature to above 100° leads to evolution of acetylene and methane, with a small amount of hydrogen. The acetylene had a higher C^{14} content, as compared with that of the ethane. Determination of the C^{14} content of the methane showed that it was formed chiefly from the carbon of the second portion of adsorbed acetylene. The higher the temperature, the lower is the C^{14} content of the methane. Thus the methane collected over the interval $100-200^\circ$ contains $10 \pm 1\%$ of its carbon derived from labelled acetylene, while in the following three portions evolved at temperatures up to 500° , the C^{14} content falls to zero. Less than half of the carbon of adsorbed acetylene is found in the gases released at up to 500° , nor do they contain any carbon derived from the first portion of acetylene adsorbed.

This experiment shows clearly that methane is formed at active centers of intermediate, but not of minimum, activation energies, these energies being lower than for those associated with reversible adsorption of acetylene, at which hydrogenation also proceeds. It appears from experiments 14 and 12 that hydrogenation proceeds for the given specimen of nickel at adsorptional active centers corresponding with 42-48% saturation of the surface. At higher saturation acetylene is reversibly adsorbed, but does not enter into reaction, while at

* The catalyst, having pyrophoric properties, was usually stored under water.

TABLE 1

Expt. No.	Sample No.	% Content of labelled acetylene carbon	Gas	Temp. °C	Amount of carbon removed from adsorption	Method of removal	Conditions of adsorption of acetylene
12	1	57±2	Ethane + acetylene	Room	4.6	Hydrogenation	Weight of catalyst 0.65 g
	2	Not analyzed	Ditto	Ditto	0.76	"	I. 2.81 ml of ordinary acetylene adsorbed; saturation of surface 45.3%
	3	96±1	Acetylene	120-150	—	Heating, + H ₂	II. 1.23 ml of labelled acetylene adsorbed; saturation of surface 19.8%
	4	Not analyzed	Methane + H ₂	200	—	Heating	
	5	"	Ditto	300	—	Ditto	
	6	3±0.3	"	400	—	"	
13	1	40±1	Acetylene	Room	4.0	Desorption	Weight of catalyst 0.65 g, from Experiment 12
	2	34±3	Ethane + acetylene	Ditto	2.4	Hydrogenation	I. 0.328 ml of labelled acetylene adsorbed; 15.7% of total adsorbed acetylene.
	3	60±1	Acetylene	50-100	9-10	Desorption	II. 1.142 ml of ordinary acetylene adsorbed; 54.6%
	4	10±1	Methane + H ₂	100-200	10	"	
	5	5±0.7	Ditto	200-380	8	"	
	6	1±0.2	"	400	4	"	
	7	0	"	485	5	"	III. 0.619 ml of labelled acetylene adsorbed; 28.2% of amount adsorbed, mean content of labelled acetylene 46%
	8	Not analyzed	"	500	2	"	
14	1	24±1	Acetylene	Room	—	Desorption, 15 hrs.	Weight of catalyst 0.4796 g
	2	15±2	Ethane + acetylene	Ditto	—	Hydrogenation 4 hrs	I. 0.92 ml of ordinary acetylene adsorbed; 20% saturation of surface
	3	28±1	Ditto	"	—	Hydrogenation 15 hrs	II. 1.019 ml of labelled acetylene adsorbed; 22% of surface occupied
	4	8±0.4	Acetylene	20-175	—	Heating, + H ₂	III. 0.545 ml of ordinary acetylene adsorbed; 10% of surface occupied; mean content of labelled acetylene 41%
15	1	37±1.6	Acetylene	Room	—	Desorption	Catalyst from experiment 14 I. 1.37 ml of labelled acetylene adsorbed
	2	20±2	Ethane	Ditto	—	Hydrogenation	II. 0.224 ml of ordinary acetylene adsorbed; average content of labelled acetylene 85.8%

lower saturations methane is formed. Acetylene adsorbed on the most active centers, in the region of small saturations, undergoes a transformation as a result of which hydrogen is evolved on heating, and a carbide type of carbon-nickel bond is formed.

TABLE 2

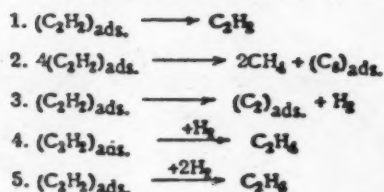
Expt. No.	Sample No.	% Content of labelled acetylene carbon	Gas	Temp., °C	Method of removal	Conditions of adsorption of acetylene
6	1	25±2	Acetylene	Room	Desorption	Weight of catalyst 0.5 g
	2	13±0.6	Ethane	Ditto	Hydrogenation	I. 0.589 ml of labelled acetylene adsorbed; saturation of surface 12%
	3-4	Not analyzed		Room-100	Desorption	II. 0.196 ml of ordinary acetylene adsorbed; saturation of surface 4%
	5	27±9	Methane + H ₂	350	Ditto	
	6	46±1.5	Ditto	450	"	Mean content of labelled acetylene 75%
7	1	14±0.8	Ethane	Room	Hydrogenation	Weight of catalyst 0.5 g
	2	11±1	Ditto	Ditto	Ditto	I. 0.365 ml of labelled acetylene adsorbed; saturation of surface 8%
	3	35±2	Methane	450	Desorption	II. 0.156 ml of ordinary acetylene adsorbed; saturation of surface 3%. Mean content of labelled acetylene 70%

Table 2 presents the results of two similar experiments, in one of which the catalyst was first dried in a stream of nitrogen before being introduced into the reaction vessel. The object of the experiments was to determine the order of magnitude of the activation energy of adsorption of acetylene at hydrogenation centers. The experiments were performed as described above. A 0.5 g sample of catalyst was placed in the reaction vessel, and was reduced with hydrogen before the experiment, at 450° in experiment 16, and at 300° in experiment 17, with subsequent degassing at the same temperatures. As appears in Table 2 it is the acetylene of the second portion which undergoes hydrogenation in both cases. The saturation of the surface is in these experiments much lower than in the preceding ones, in accordance with the lower adsorptive activity of the given specimen.

The experiments show that hydrogenation proceeds basically at active centers corresponding with a 12-16% saturation of the surface, and with an activation energy of 15-16 kcal/mol, as found from adsorption measurements.

3. Discussion of results

The above-described experiments show that the active surfaces of the catalysts examined contain active centers which differ from each other in respect of their activation energies and heat of adsorption, as well as of their catalytic properties. We observed the following reactions of acetylene adsorbed on metallic nickel:



The first three processes took place during desorption of acetylene at room temperature.

(a) Reversible adsorption of acetylene. When we adsorbed two portions of acetylene, of which one contained labelled carbon, we found that the first portion of acetylene desorbed at room temperature consisted of both portions, in various proportions. Successive portions desorbed at higher temperatures consist to an increasing extent of the second fraction of acetylene adsorbed. In experiment 13 the first fraction desorbed at room temperature contained 40% of the last adsorbed fraction of acetylene. The second portion, desorbed at 50-100°, contained 60±1% of this fraction. In experiment 14, the first portion desorbed at room temperature contained 70%, and the second, desorbed at 175°, 92% of the last adsorbed fraction of acetylene.

Thus desorption does not begin with the active centers of maximum $E_{ads.}$ at which adsorption takes place last, but with the more active centers, corresponding with lower saturation of the active surface. This is evidence of the complex nature of the relation between activation energy of adsorption and desorption. Fig. 2 represents one of the possible variants of the relation between $E_{ads.}$ and $E_{des.}$ explaining the effects observed.

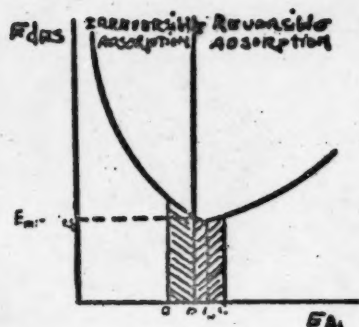


Fig. 2. Schematic representation of the relationship between energy of activation of desorption $E_{des.}$ and of adsorption $E_{ads.}$. Region a-b: methane forming centers; b-c hydrogenating center.

(for an exponential type of function of distribution of active centers according to $E_{ads.}$), the content of acetylene derived from the last portion adsorbed will increase in successive desorbed fractions of acetylene; this was in fact confirmed by experiment.

The region of reversible adsorption on an active specimen is at a saturation of 45%. In experiment 12 the boundary between the first and the second portions adsorbed (of which the second contained labelled C^{14}) is at 45% saturation. The first fraction of the hydrogenation product, which usually differs little from the first desorbed product with respect to its C^{14} content, contains 57% of acetylene of the last portion adsorbed. It follows that the adsorption boundary between the two portions of acetylene is in this experiment close to the saturation value corresponding with minimum desorption activation energy values. Since the velocity of desorption is determined by the value of desorption activation energy, succeeding fractions of desorbed gas should contain acetylene from active centers of activation energy both higher and lower than E_p . However, irreversible adsorption takes place in the region of low activation energy; here the adsorbed acetylene either undergoes decomposition or enters into reaction faster than it can be desorbed from the surface. In view of this succeeding portions of desorbed gas will contain more of the acetylene which had been adsorbed on centers of high activation energy, i.e., more of the acetylene adsorbed from the second portion.

The acetylene desorbed at 120-150° in experiment 12 contains 90% of the acetylene from the second portion adsorbed. In experiment 14 the boundary of adsorption between succeeding portions is at 42% saturation, i.e., at a lower saturation than that corresponding with $E_{min.des.}$. Accordingly, the acetylene desorbed at room temperature contains 75% of acetylene from the last adsorbed portion, i.e., more than in experiment 12. The fraction desorbed at higher temperatures, up to 175° as in experiment 12, contains 92% of acetylene from the last adsorbed portion.

The experimental data thus agree with the assumed relationship between $E_{ads.}$ and $E_{des.}$. We have already encountered this type of relationship when studying the kinetics of desorption of activated adsorbed hydrogen on sugar charcoal [8]. In that case this character was even better defined, giving rise to a series of anomalies in the kinetics of desorption, and leading to appearance of "retention zones" in adsorption on charcoal which had been partly degassed after adsorption thereon on hydrogen. We would add that such a connection between energy of activation of adsorption and desorption may occur when the distribution functions of active centers according to activation energies and heats of adsorption are not of the same type. This in turn requires that the linear

The minimum activation energy of desorption corresponds with the value of activation energy E_p . At low levels of saturation, not attaining the minimum values of activation energy of desorption, desorption begins at the active centers having the maximum energies of activation of adsorption; at saturation levels exceeding this value desorption will, irrespective of the saturation level, take place first of all at the active centers for which the value of $E_{ads.} = E_p$. In the case of adsorption of two portions of acetylene, of which one is labelled with C^{14} , the ratio of labelled to ordinary acetylene in the desorbed gas will depend on how much of the active surface has been filled by the first portion, with relation to saturation corresponding with minimum values of activation energy of desorption. If the adsorption boundary between the two portions lies to the right of the saturation value corresponding with $E_{min.des.}$ then the first desorbed fraction will contain acetylene originating from the portion first adsorbed, while if to the left it will originate from the second portion. If the boundary lies close to the saturation value corresponding with $E_{min.des.}$ then the first and all succeeding desorbates will be made up of both adsorbed portions. In this, in view of the proportionality of $E_{ads.}$ to the logarithm of saturation

relation postulated by certain authors between activation energy and heat of adsorption should not be present.

(b) Additional experiments were performed, dealing with the kinetics of hydrogenation and adsorption of acetylene, in order to establish whether the adsorptional mechanism of hydrogenation is basic to the process. This was shown to be the case, and a group of hydrogenating centers was found in the catalyst which determined the kinetics of the reaction. The results obtained from the study of the active surface by the differential isotope method, and from the kinetic study permit of the drawing of definite conclusions regarding the mechanism of formation of methane and of hydrogenation; these will be considered in the next paper.

The author has pleasure in expressing his gratitude to S. Z. Roginsky for his valuable advice, and for the interest he took in the carrying out of this research.

SUMMARY

1. The active surface of a nickel catalyst is not uniform with regard to activation energy of adsorption of acetylene.

2. Hydrogenation of acetylene takes place at certain of the centers which adsorb acetylene reversibly. These centers occupy 4-6% of the surface, at the boundary between reversible and irreversible adsorption.

Formation of methane takes place at active centers with higher heats of adsorption. Decomposition of acetylene with liberation of hydrogen takes place at the active centers with the highest heats of adsorption.

3. The non-linear nature of the relation between E_{ads} and E_{des} is established.

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Institute of Physical Chemistry
Academy of Sciences USSR

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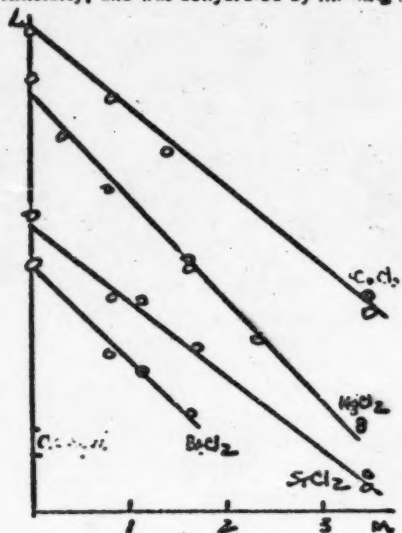
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COORDINATION NUMBERS OF THE IONS Mg^{2+} , Ca^{2+} , Sr^{2+} , AND Ba^{2+} IN AQUEOUS SOLUTIONS

O. Ya. Samoilov

It was thought to be of interest to extend to bivalent ions the results described in our previous paper [1] for univalent ions, and to determine the integral heats of dissolution of Mg, Ca, Sr, and Ba chlorides in aqueous HCl.

The salt $MgCl_2 \cdot 6H_2O$ was prepared by storing the commercial salt (analytically pure) in a desiccator over 68% sulfuric acid at 20°, to constant weight, which was usually achieved in about 6 weeks. Calcium, strontium, and barium chloride were taken in the anhydrous form; strontium and barium chloride (chemically pure) were dehydrated by heating their mixtures with chemically pure ammonium chloride (in order to avoid hydrolytic decomposition) until all the NH_4Cl was eliminated. Calcium chloride dihydrate was prepared similarly, and was dehydrated by melting in a platinum crucible.



Integral heats of dissolution of $MgCl_2$, $MgCl_2 \cdot 6H_2O$, $CaCl_2$, $SrCl_2$, and $BaCl_2$ in aqueous HCl

The amounts of the salts taken for the calorimetric experiments were such that the concentrations obtained (constant for each salt) were from 0.03 to 0.06 g. mole of salt per 50 g. mole of water. The integral heats of dissolution were measured in a calorimeter with an outer jacket maintained at a temperature of $25 \pm 0.01^\circ$. The methods used in making the measurements were identical with those described in an earlier paper [2]. After weighing out samples of $MgCl_2 \cdot 6H_2O$ the tube with the salt was replaced in the desiccator for 2-3 days, until the weight became constant.

The results of determination of integral heats of dissolution are given in Table 1, and are represented in the graph. The concentration of acid m is expressed as g.-mole HCl per 50 g.-mole water, and the heat of dissolution L as kg.-cal per mole of salt. The curves are distributed along the ordinate axis (retaining the same scale). The heats of dissolution of $BaCl_2$ are given only up to a HCl concentration of 1.65, in view of the low solubility of this salt in hydrochloric acid. The various determinations of L were accurate to within 1% on the average; the low heats of dissolution of $MgCl_2 \cdot 6H_2O$ were an exception to this.

Table 2 gives the values of B (cal/mol 1 m) for the salts studied ($B = -\Delta L/\Delta m$; $\Delta L/\Delta m$ are derived from experimental results by the method of least squares).

Inasmuch as the ions under examination are bivalent the values of B should be halved, in order to find the coordination numbers from equations (2) or (3) [1]. If we write equation (2) for $CaCl_2$ as

$$K \left(\frac{2n_{Ca^{2+}}}{r_{Ca^{2+}} + 1.38} - \frac{2n_{Cl^-}}{r_{Cl^-} + 1.38} \right) = B; \quad (1)$$

the figure 2 in the first term is connected with the charge of Ca^{2+} , and in the second term with the circumstance that each mole of the dissolved salts gives rise to two g. ions of Cl^- . If we divide equation (1) by 2 we see that the coordination number of bivalent ions is found in the same way as for univalent ions, with the difference that instead of B we take $B/2$.

TABLE 1

Integral heats of dissolution of salts in aqueous HCl at 25°

Dissolved salt	Concentration of HCl in moles per 50 moles water	Heat of dissolution in Kcal per mole of salt	Dissolved salt	Concentration of HCl in moles per 50 moles water	Heat of dissolution in Kcal per mole of salt
MgCl ₂ ·6H ₂ O	0.00	+3.40	CaCl ₂	3.51	+16.71
	0.32	+2.91		3.51	+16.88
	0.81	+2.45	SrCl ₂	0.00	+11.82
	1.63	+1.84		0.84	+11.13
	1.63	+1.78		1.12	+11.09
	2.37	+1.19		1.68	+10.70
	3.40	+0.48		3.46	+ 9.62
	3.40	+0.43		3.46	+ 9.52
CaCl ₂	0.00	+19.12	BaCl ₂	0.00	+ 2.84
	0.84	+18.54		0.81	+ 2.06
	1.70	+18.09		1.12	+ 1.91
				1.65	+ 1.55*

* Measurements made with a second specimen of BaCl₂ gave values for \bar{L} at this concentration equal to +1.71 and +1.72 Kcal /mole, but measurements relating to a single series were taken for the curve.

TABLE 2

Values of β for the salts studied

Salt	MgCl ₂	CaCl ₂	SrCl ₂	BaCl ₂
β	897	666	636	780

$$K \left(\frac{n_{Ca^{2+}}}{i_{Ca^{2+}} + 1.38} - \frac{n_{Cl^-}}{i_{Cl^-} + 1.38} \right) = \frac{\beta}{2} \quad (1')$$

It should first of all be noted that the coordination number of Mg²⁺ in aqueous solutions is practically equal to that of the Li⁺ ion; for MgCl₂ $\beta/2 = 448$, and for LiCl $\beta/2 = 465$ [1] (the values differ by about 4%). This appears to be connected with the equality of the coordination numbers in solution, and not simply with an equality of crystallochemical radii

(electrostatic equivalence of Li⁺ and $\frac{1}{2}$ MgCl₂²⁺).

The natural conclusion to be drawn from this is that the ions Li⁺ and Mg²⁺ have a coordination number of 6 in aqueous solution; this is the maximum possible in connection with the relation of the radius of these ions to that of water molecules. It has, however, been shown [1] that the upper limit of possible values for the coordination number of the Li⁺ ion is 4.23, so that this conclusion must be rejected.* Apparently the closeness of a number of properties of the Li⁺ and Mg²⁺ ions in aqueous solution is responsible for the effect.

Taking $K = 1.17 \cdot 10^8$ and $n_{Cl^-} = 4.4$ [1] we can derive the coordination numbers of the ions Mg²⁺, Ca²⁺, Sr²⁺, and Ba²⁺ in aqueous solutions at 25° from the values of $\beta/2$. These numbers (n) are given in Table 3.

TABLE 3

Coordination numbers in aqueous solution (n) and ρ^* for the ions Mg²⁺, Ca²⁺, Sr²⁺, and Ba²⁺ at 25°

Ion	Mg ²⁺	Ca ²⁺	Sr ²⁺	Ba ²⁺
n	3.8	4.0	4.4	4.8
ρ^*	0.065	0.054	0.050	0.048

The coordination numbers rise from the ion Mg²⁺ to the ion Ba²⁺; we know that the energy of hydration of these ions falls in the same order. This shows the difference between coordination numbers of ions and their so-called hydration numbers. If, however, we calculate the surface density of packing of water molecules in the first coordination layer of the ions, ρ^* , suggested previously as an indicator of hydration [1], we see that the value of ρ^* falls from Mg²⁺ to Ba²⁺, although it remains greater than for water **. This is as could be expected, as we know that the given ions are hydrated.

* This is confirmed in the determination of the coordination number of the ion Be²⁺ in aqueous solutions.

** At 25° $\rho_{H_2O}^* = 0.044 \text{ \AA}^{-2}$ [1].

As in the case of the ions Li^+ , Na^+ , K^+ , Cl^- , Br^- , and I^- , examined in an earlier paper, the coordination numbers are close to the mean value for the coordination number of water molecules in water. It may be concluded that the structure of water determines the structure of dilute aqueous electrolyte solutions.

The modification by ions of the structure of water is connected, in the first place, with introduction into water of particles whose radius differs from that of water molecules, in the second place, with the difference between the coordination numbers of the ion and of water molecules (should such a difference be found), and in the third place with the re-ordering of the molecules of water closest to the ion. It is evident that of the factors enumerated the second is the most important energetically, inasmuch as the effect of the change in coordination number is exerted at a great distance. It appeared that only a very small change takes place in the coordination number, or possibly none at all.

Coordination numbers of the order of 6 could be peculiar to the ions, in accordance with their distribution in vacant positions of the structure of water. Such coordination numbers were not, however, encountered. This is as would be expected, if the re-orienting effect exerted by ions on surrounding molecules of water is taken into account; this re-orientation is of greater magnitude in vacancies in the structure of water, surrounded by 6 molecules of water, than in their absence. The structure of dilute solutions in which the ions are surrounded by water molecules represents the least modification of the structure of water.

The general conclusion drawn agrees with the results of roentgenographic examination of aqueous solutions of LiCl , LiBr , and RbBr as reported by Beck [3], who found that on the curves representing intensity of scattering of X-rays by solutions of LiBr or RbBr (concentrations 4.0 and 2.58 M, respectively) the peak due to scattering by pure water is the prevailing one. Since at these concentrations scattering due to the ions considerably exceeds that due to water, Beck draws the conclusion that the ions are arranged in these solutions similarly to water molecules, i.e., they are distributed in the structure of water in such a way that they "replace" its molecules. We cannot speak literally of the replacement by ions of water molecules; the ions modify the arrangement of the adjacent water molecules, and the relative orientation of molecules (orientation of tetrahedrally arranged negative and positive poles of the molecules) is the determining factor for the structure of water. It is scarcely permissible to draw any analogy with solid solutions, however. We would add that Bernal and Fowler [4] took the coordination number of bivalent ions as being 6, on the basis of calculation of the energy of coordination by ions of molecules of water in solutions; Eley and Evans [5] came to a similar conclusion.

According to Beck [3] the structure of very concentrated solutions (e.g., 13 M) of LiCl or LiBr is similar to that of the appropriate hydrated salt, i.e., the molecules of water are arranged together with the ions of which the salt structure is made up. Beck's conclusion is probably of general applicability, and Mathieu and Lounsbury [6] arrived at the same conclusion on the basis of a study of Raman spectra of concentrated aqueous nitrates.

The question arises in what way the transition between these two states takes place (structures of dilute and concentrated solutions). A continuous transition is possible [6] *; however, the work of Danilov and his co-workers has established the existence of a eutectic structure in a number of liquid solutions. Similarly, the study of scattering of X-rays by molten alloys which give eutectic phase diagrams has led to the conclusion that they contain groupings with the structures of both one and the other component [7]. The existence of such groupings has also been established in aqueous solutions of acetone [8]. It is evident that in a number of liquid systems consisting of the molecules A and B the combinations AA and BB may be more probable energetically than the combination AB [9].

Aqueous solutions of electrolytes may also, within certain ranges of temperature and concentration, possess a eutectic structure, in this meaning of the term. Depending on the temperature, the structure of solutions resembles one or another of their components, as the concentration is increased (the structure of water in dilute, and of the solid hydrate in concentrated, solutions). These structures only gradually undergo deformation [10], and further change in concentration leads to the appearance of a eutectic structure.

A relationship of this sort appears to be suggested by the results of a study of the dependence on temperature of the intensity of scattering of X-rays by NaCl and LiCl solutions, of a composition close to the eutectic, reported by Danilov and Neimark [11], who found that at low temperatures the second maximum of the intensity of scattering curve for water, which is barely perceptible at room temperature, reappears. According to these authors this may be due to appearance of concentration inhomogeneities in the solutions at low temperatures, when those parts of it which gain water assume its structure.

* A continuous transition is achieved at excessively low temperatures.

SUMMARY

1. Integral heats of dissolution of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$, CaCl_2 , SrCl_2 , and BaCl_2 in aqueous HCl of various concentrations, at 25°, have been determined in a calorimeter with an isothermic envelope.

2. Coordination numbers have been found, using the method previously described, for aqueous solutions of the ions Mg^{2+} , Ca^{2+} , Sr^{2+} , and Ba^{2+} . The values are close to 4, and they rise from Mg^{2+} to Ba^{2+} . The mean density of distribution of water molecules around the ions diminishes from Mg^{2+} to Ba^{2+} .

3. The structure of dilute aqueous solutions of electrolytes is determined largely by the structure of water.

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N. S. Kurnakov Institute of General and Inorganic
Chemistry
Academy of Sciences USSR

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STUDY OF SYSTEMS CONTAINING HYDROGEN PEROXIDE

PART 2. THERMAL PROPERTIES AND DEHYDRATION OF PERHYDRATES OF SODIUM CARBONATE

S. Z. Makarov and V. N. Chamova

It was shown in the preceding paper [1] that the following phases are formed in the system $\text{Na}_2\text{CO}_3\text{-H}_2\text{O}_2\text{-H}_2\text{O}$ at 0-20°: $\text{Na}_2\text{CO}_3\cdot\text{H}_2\text{O}\cdot 1.5\text{H}_2\text{O}_2$; $\text{Na}_2\text{CO}_3\cdot\text{H}_2\text{O}\cdot 2\text{H}_2\text{O}_2$ and $\text{Na}_2\text{CO}_3\cdot 2\text{H}_2\text{O}_2$.

Specimens of these compounds were subjected to thermal analysis, with differential registration on a registering pyrometer of the N. S. Kurnakov type. The heating curve of $\text{Na}_2\text{CO}_3\cdot\text{H}_2\text{O}\cdot 1.5\text{H}_2\text{O}_2$ (Fig. 1) shows two inflections, due to an endothermic effect at 105° and to an exothermic one at 120°. The endothermic effect corresponds with dehydration, with formation of the anhydrous perhydrate, and the exothermic one with decomposition of the anhydrous perhydrate, with evolution of oxygen.

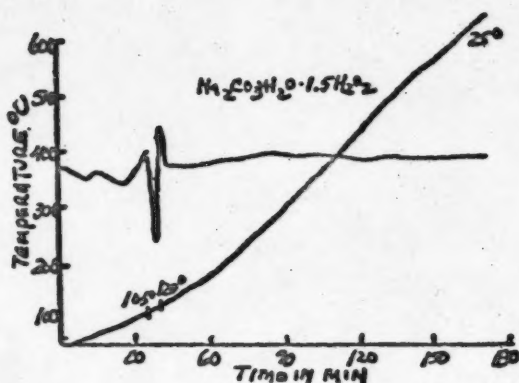


Fig. 1.

The results of analysis of the original substance and of the products of heating at 105-110° and at 120° are given in Table 1... We see that the process begins with dehydration, followed by decomposition of perhydrol of crystallization.

The heating curve of the compound $\text{Na}_2\text{CO}_3\cdot\text{H}_2\text{O}\cdot 2\text{H}_2\text{O}_2$ (Fig. 2) is similar, and shows an endothermic effect at 95°, and an exothermic one at 125°. The salt had initially the % composition:

Na_2CO_3	55.32
H_2O_2	36.38
H_2O	8.30

The nature of the heating curves indicates a means of obtaining anhydrous perhydrates of sodium carbonate from the corresponding hydrated salts, viz., by dehydrating at temperatures

below the exothermic decomposition point. This also affords confirmation of our previously made conclusion regarding the perhydrate nature of the type of peroxide compounds.

TABLE 1

Substance	Content %		
	In original substance	at 105-110°	at 120°
Na_2CO_3	62.75	75.75	99.95
H_2O_2	30.32	22.14	—
H_2O	6.93	2.11	1.0

We found that the compounds $\text{Na}_2\text{CO}_3\cdot 1.5\text{H}_2\text{O}_2$ and $\text{Na}_2\text{CO}_3\cdot 2\text{H}_2\text{O}_2$ were in fact obtained by heating the hydrates at appropriate temperatures, and at reduced pressures (8-10 mm).

The dehydrated perhydrate $\text{Na}_2\text{CO}_3\cdot 2\text{H}_2\text{O}_2$ gives a sharply defined exothermic effect on the heating curve (Fig. 3) at 50°, associated with evolution of oxygen, and gives a second, endothermic effect at 140°.

TABLE 2

Composition	Content %		
	Na_2CO_3	H_2O_2	H_2O
Original $\text{Na}_2\text{CO}_3\cdot\text{H}_2\text{O}\cdot 1.5\text{H}_2\text{O}_2$	62.75	30.32	6.93
	60.57	29.15	10.28
Dehydrated $\text{Na}_2\text{CO}_3\cdot 1.5\text{H}_2\text{O}_2$	68.18	32.30	—
Theoretical $\text{Na}_2\text{CO}_3\cdot 1.5\text{H}_2\text{O}_2$	67.42	32.44	—
Original $\text{Na}_2\text{CO}_3\cdot\text{H}_2\text{O}\cdot 2\text{H}_2\text{O}_2$	55.32	36.38	8.30
Dehydrated $\text{Na}_2\text{CO}_3\cdot 2\text{H}_2\text{O}_2$	60.33	40.52	—
Theoretical $\text{Na}_2\text{CO}_3\cdot 2\text{H}_2\text{O}_2$	61.00	39.00	—

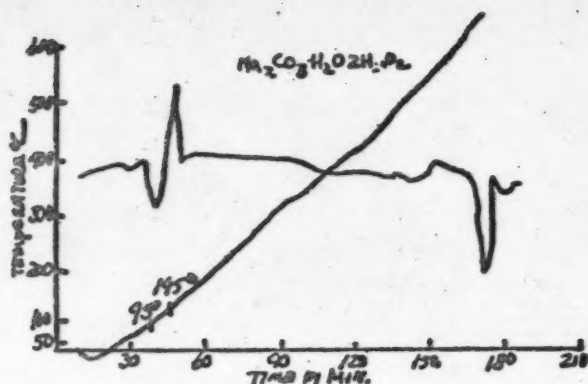


Fig. 2

salts obtained from sodium carbonate and aqueous perhydrol, by heating at temperatures below those of the exothermic effects, in vacuum.

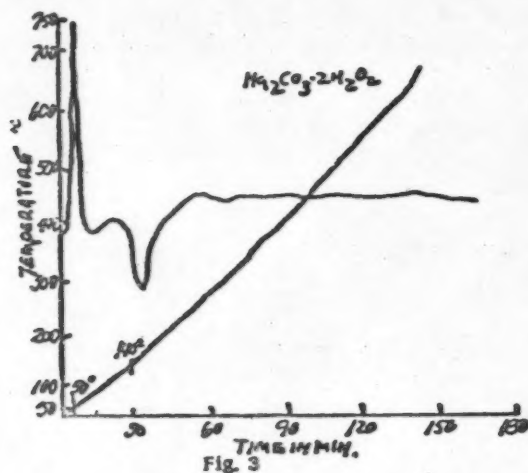


Fig. 3

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Laboratory for Peroxide Compounds
Academy of Sciences USSR

LITERATURE CITED

- [1] S. Z. Makarov and V. N. Chamova, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, No. 3, 255 (1951).

SUMMARY

1. Heating curves with differential registration, using a registering pyrometer, are constructed for the perhydrates $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O} \cdot 1.5\text{H}_2\text{O}_2$ and $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O} \cdot 2\text{H}_2\text{O}_2$. The curves have two inflections, the first being due to an endothermic effect, associated with dehydration, and the second to an exothermic effect, due to thermal decomposition of perhydrate, with evolution of oxygen.

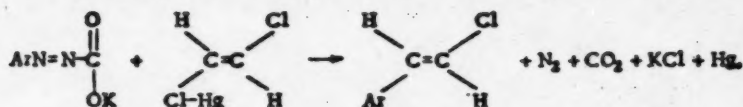
2. The anhydrous perhydrates $\text{Na}_2\text{CO}_3 \cdot 1.5\text{H}_2\text{O}_2$ and $\text{Na}_2\text{CO}_3 \cdot 2\text{H}_2\text{O}_2$ may readily be prepared from the hydrated

MECHANISM OF REACTION OF MAGNESIUM ALKYL HALIDES WITH β -SILICOALKYL HALIDES*

A. D. Petrov and V. F. Mironov

β -Silicoalkyl halides (--Si--C--C--X) closely resemble, as regards their structure and chemical behavior,

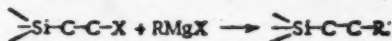
the β -halides of a series of organometallic halides (M--C--C--X), of which a detailed study has been made by Nesmeyanov and co-workers [1]. These authors showed that a typical member of this series, Biginelli's complex (ClHgCH=CHCl), may undergo decomposition when treated with certain reagents, such as $\text{C}_6\text{H}_5\text{MgBr}$, to give acetylene and mercuric chloride, from which it was prepared, while in other cases the acetylene of the complex reacts with the reagents forming new C-C bonds. The following reaction illustrates this:



This reaction enables us to synthesize the formerly difficultly preparable *cis*- ω -chlorostyrenes. The metal, in this case mercury, is eliminated, and is not present in the reaction product. Reactions are, however, also known in which the metal remains attached to the product, but this is usually found for reactions affecting the halogen atom attached to the metal, and not in the β -position with respect to it. An example is given by the reaction described by the Indian scientist [2]:



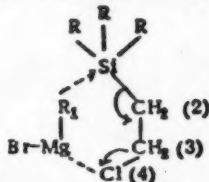
We were able to find the conditions under which β -silicoalkyl halides only partly undergo decomposition, the main reaction being with the halogen in the β -position to the silicon, by the general scheme:



This opens up new perspectives for the synthesis of silicohydrocarbons and of silicon-organic compounds in general. The majority of the silicohydrocarbons now known were prepared by the Wurtz or the Grignard-Wurtz reaction from silicoalkyl halides in which the halogen is attached to the silicon atom. Silicoalkyl halides in which the halogen atom is in the α -, β -, or γ -position to the silicon have only recently become known. The first β -silicoalkyl halide was β -chloroethyltriethylsilane, $(\text{C}_2\text{H}_5)_3\text{SiCH}_2\text{CH}_2\text{Cl}$, prepared in 1937 by Ushakov and Itenberg [3], who also showed that it differs sharply from α -halides in its instability in dilute aqueous alkalis. Whitmore and co-workers [4], in studying the reactions and properties of β -silicoalkyl halides, in the cases of certain primary β -chlorides, found that they underwent cleavage of the Si-C bonds when taken for the Grignard-Wurtz synthesis:

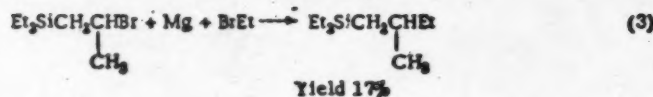
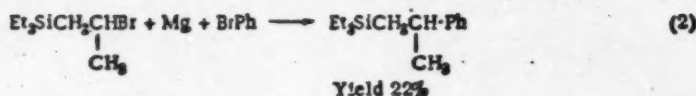
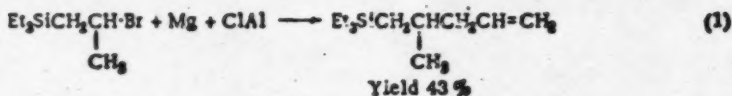


They represented the mechanism of cleavage at the Si-C bonds, the so-called β -decomposition, as a cyclic process, proceeding in the six-membered coordination complex:



* A lecture given at a general meeting of the Division of Chemical Sciences of the Academy of Sciences USSR, on March 28, 1962.

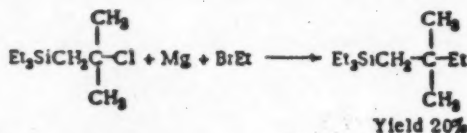
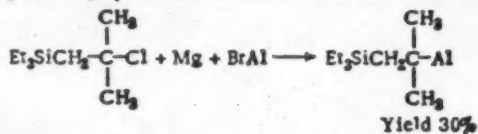
In this complex the Si atom and the radical R_1 of the Grignard reagent are in the 1-6 positions. The Si atom attracts an electron pair belonging to the radical R_1 , and at the same time transposition of the electrons of the 2nd and 3rd carbon atoms takes place. The process leads to formation of a new R_1 -Si bond, with simultaneous formation of MgX_2 and ethylene. The work of these American scientists has led to the acceptance of the view that β -silicoalkyl halides are quite useless as intermediates for syntheses, in particular for those based on the Grignard-Wurtz reaction. Thus, for example, Sommer and Marans [5] draw attention in a paper published in 1950, to the instability of compounds containing halogen, hydroxyl, or other functional groups in the β -position, and they recommend the use of compounds with the functional group at a greater distance from the Si, such as the γ -position. In arriving at these aprioristic assumptions the American authors neglected to take into consideration the structure of either the β -silicoalkyl halide or of the compounds with which it reacts, and greatly over-emphasized the importance of the β -influence. We have shown in two of our papers [6] that these authors were unduly pessimistic regarding the synthetic possibilities of β -silicoalkyl halides. In the first of these papers we described the reactions:



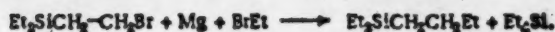
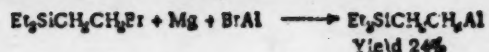
It was possible to carry out these reactions because the β -silicoalkyl halides, which are highly sensitive to thermal factors, were prepared and stored at low temperatures until they were taken for the reactions. A study of the behavior of β -silicoalkyl halides in a number of different reactions showed that whether or not β -decomposition or synthesis takes place at a C-X bond depends on a number of factors. In the first place, the direction in which the reaction proceeds depends on the nature of the RMgX compound used. Active magnesium alkyl or aryl halides (allyl, phenyl) favor the transfer of the whole reaction to the C-X bond, whereas in the cases of BrMgEt or BrMgMe the reaction takes place at both the C-X and the Si-C bonds. But the direction of the reaction also depends on the nature of the halogen-containing group in the β -position to the silicon atom; secondary β -silicoalkyl halides are more resistant to β -decomposition than are primary ones, and it was later found that tertiary ones are even more resistant.

In our second paper we studied the effect of the nature of the halogen, and also investigated the reactions of various Grignard reagents with tertiary and primary β -silicoalkyl halides. It was found that the use for the syntheses of secondary β -chlorosilanes instead of the corresponding β -bromides gave yields 1.5 times greater.

Attempts to prepare the tertiary β -bromide or β -iodide by adding HBr or HI to $\text{Et}_3\text{SiCH}_2\text{C}(\text{CH}_3)=\text{CH}_2$ at 70° were unsuccessful, but the chloride was obtained similarly, by addition of HCl . This chloride reacted with RMgX , where R is allyl or ethyl (some β -decomposition in the latter case):



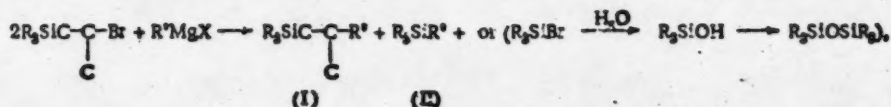
We then added HBr to $\text{Et}_3\text{SiCH}=\text{CH}_2$, and condensed the primary β -bromide so obtained with MgBrAl or MgBrEt :



In the latter case only traces of triethylbutylsilane were obtained, the main product being Et_3Si , by β -decomposition.

Having investigated the effect of the nature of the Grignard reagent and of the halogen-containing radical on the strength of the Si-C bond and of transfer of reactivity to the C-X bond, we next studied the effect of the radicals attached to the Si atom. With this object we decided to prepare a series of trialkyl- (and arylalkyl)-allylsilanes R_3SiAl , and to study the reactions of the β -bromides prepared therefrom with Grignard reagents, in order to find in which cases the reaction of synthesis prevails, and in which the dominating reaction is that of β -decomposition.

In this way, for the reaction which for secondary β -silcoalkyl bromides may be represented by the equations:



we have to find the ratio of (I) to (II) in the products. The following 7 allylsilanes were prepared: Ph_3SiAl , Ph_2MeSiAl , PhMe_2SiAl , Me_3SiAl , Et_3SiAl , Pr_3SiAl and Bu_3SiAl ; the yields were about 50% when the radicals attached to the Si atoms contained an odd number of carbon atoms, and about 80% when this number was even.

TABLE 1

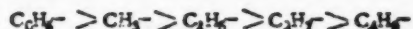
Yields of $\text{R}_3\text{SiCH}_2\text{CH}(\text{CH}_3)\text{R}'$, as %
calculated on initial $\text{R}_3\text{SiCH}_2\text{CH}=\text{CH}_2$

R \ R'	Et	Pr	Ph	Al
PhMe ₂	5	—	—	24
Me ₃	5	6	9	35
Et ₃	12	25	23	50
Pr ₃	12	20	—	38
Bu ₃	20	—	—	50

We were not able to perform any syntheses with the first of these allylsilanes, owing to the readiness with which it polymerizes. β -Bromopropyltrialkylsilanes were prepared from the remaining 6 trialkyl (or triarylalkyl)-silanes, in the usual way, at -70° . The β -bromides were added to a 2-3 fold excess of $\text{R}'\text{MgX}$. The reaction with allyl bromide was conducted according to Yavitsky. The results of the syntheses are presented in Table 1, from which it appears that the yields of alkylsilanes are 2-4 times greater for β -bromides with a SiEt_3 group than with a SiMe_3 group. Moreover, partial β -decomposition is here observed even with AlMgBr , which does not cause β -decomposition of even the least stable primary β -bromide (in the case of $\text{Et}_3\text{SiCH}_2\text{CH}_2\text{Br}$). The smaller yield of silanes from trimethyl- than from triethyl- β -bromopropylsilane suggests that β -decomposition results not so much from thermal instability of the β -silcoalkyl halides, as the first of these halides is

considerably more heat resistant than is the second, as from the reactivity of the C-X bond (determined by the influence of all the atoms entering into the β -silcoalkyl halide). Evidence supporting the view that thermal stability should be distinguished from chemical stability of β -silcoalkyl halides is also to be found in the literature.

Thus it is evident from the work of Whitmore et al. [7] that $\text{Cl}_3\text{SiC}-\text{C}-\text{Cl}$ can be distilled without decomposition at 152° , whereas $\text{Et}_3\text{SiC}-\text{C}-\text{Cl}$ decomposes at 80° [4]. Yet the former compound reacts instantaneously with 0.1 N alkali, with evolution of ethylene, while the latter reacts only very slowly. Whitmore interprets these facts as showing that β -decomposition is due to action of nucleophilic OH^- on the Si atom, and further that replacement of one chlorine atom attached to Si by R causes a ten-fold lowering of β decomposition due to CH_3 , since the presence of electronegative substituents on the Si atom renders it a more effective center of nucleophilic action [8]. It is evident that a similar effect applies to the reactions studied by us. With diminishing electronegativity of the series of radicals attached to Si

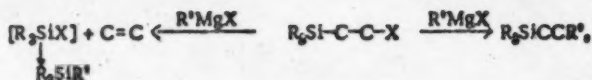


the yields of silanes obtained by condensation at the C-X bonds rise, and β -decomposition diminishes. To this we should add an additional small correction, depending on whether the radicals attached to Si have an odd or even number of carbon atoms; this affects not only the yield of trialkylallylsilanes, but also that of silanes prepared from β -silcoalkyl halides. It may also readily be foreseen that such factors as steric hindrance, which has scarcely been studied, can also affect the yields of silcohydrocarbons.

We found, further, that if to EtMgBr we add $\text{Et}_3\text{SiC}-\text{C}-\text{Br}$, and very soon after we decompose the product by

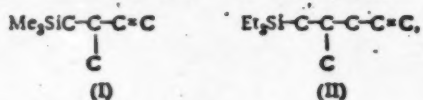
adding water, without boiling, we obtain, in addition to $\text{Et}_3\text{Si}-\text{C}-\text{C}-\text{Et}$ obtained by the Grignard-Wurtz reaction,

the silanol Et_3SiOH ; Et_3Si , the final product of β -decomposition, is practically absent. When, however, the reaction product is subjected to prolonged boiling, silanol is not produced, the by-product being Et_3Si . It is evident that Et_3Si is formed from Et_3SiBr and EtMgBr . When the time of boiling is too short Et_3SiBr does not afford Et_3Si , giving silanol instead. These observations, which were not noted by Whitmore, show that the mechanism of β -decomposition suggested by him is erroneous. The reactions of β -decomposition and of synthesis from β -siloalkyl halides can more reasonably be represented by the following simple mechanism:

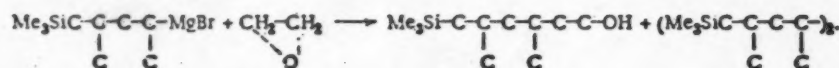


showing that the primary reaction of β -decomposition of silicoalkyl halides, as well as of metallo-organic compounds of similar type, is decomposition with formation of olefin and trialkylsilane halide, which then condenses with Grignard reagent to give a $\text{Si}-\text{R}'$ bond.

We then prepared the as yet unknown δ -siloalkyl bromides from the β -bromides. HBr adds on slowly to the appropriate silico-olefins. [In particular to compound (II)]



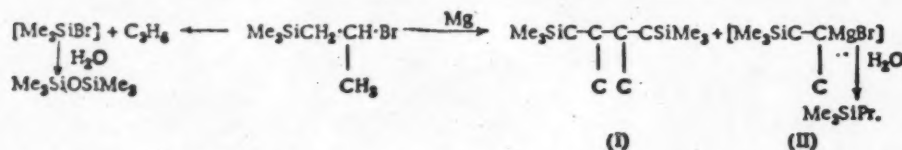
but the yields of δ -siloalkyl bromides were 90 and 84%, respectively. In distinction to the β -bromides they were weakly ionized compounds, not giving a precipitate with boiling aqueous AgNO_3 , and reacting with NaOH somewhat similarly to α -siloalkyl halides or to primary alkyl halides. Ethylene oxide reacted with one of these reagents as follows:



The yield of alcohol was 37%.

It is of interest that α - and γ -siloalkyl halides react with Mg and then with ethylene oxide to give only the corresponding alcohols. The β -bromides not only react readily with Grignard reagents, but they are also able themselves to afford such reagents, although with considerable β -decomposition and evolution of olefins.

The extent of β -decomposition may be somewhat reduced by preparing the Grignard reagents from β -siloalkyl halides at low temperatures. The reaction proceeded as follows:



In view of the thermal stability of the β -siloalkyl halide taken, its β -decomposition at room temperature might be explained as being due to activation of the decomposition reaction by the Grignard reagent formed. Compounds (I) and (II), which show that the β -siloalkyl halide forms a Grignard reagent, were isolated after treating the product with water and removing the products of β -decomposition (hexamethyldisiloxane) with concentrated sulfuric acid.

A certain similarity between β - and δ -siloalkyl halides, which differ so sharply in their thermal and chemical stability, may consist in the tendency of both of them to afford disilanes. The formation of Grignard

reagents by β -siloalkyl halides may permit of the use of the latter for the synthesis of alcohols, at least, by condensation with certain carbonyl compounds.

EXPERIMENTAL

Phenylallyldimethylsilane $C_6H_5(CH_3)_2SiCH_2CH=CH_2$ (I). A few ml of allyl bromide is added to 54 g of magnesium (2.2 moles) in 1 liter of absolute ether, contained in a 2 l. flask fitted with a reflux condenser, a stirrer, and a dropping funnel. The stirrer is switched on when reaction begins, and a mixture of 171 g of phenyldimethylsilyl chloride (1 mole) (b.p. $194.4^\circ/750$ mm; n_D^{20} 1.5080; d_4^{20} 1.0307) and 133 g of allyl bromide (1.1 mole) is added gradually during 7 hrs. The ether is distilled off during 2-3 hrs on the following day, and the solid residue is heated at 100° for 7 hrs. The ether, which had been distilled off is returned to the flask, the contents of which are treated first with water, and then with a minimum amount of 10% HCl. The ethereal extract is dried with Na_2SO_4 , the ether is distilled off and the liquid residue is fractionated, using a column with 10-15 theoretical plates, giving 144 g of phenylallyldimethylsilane, b.p. $213.6^\circ/751$ mm; n_D^{20} 1.5090; d_4^{20} 0.8911; MR_D 59.07; calculated [11] MR_D 58.89, yield 81.7%.

Found %: H 9.16; 9.17; C 75.24; 74.97; Si 15.97; 16.29
 $C_{11}H_{16}Si$. Calculated %: H 9.15; C 74.94; Si 15.92

Other allylsilanes were prepared similarly.

Diphenylallylmethylsilane $(C_6H_5)_2CH_2SiCH_2CH=CH_2$ (II), b.p. $310-311^\circ/740$ mm; n_D^{20} 1.5660; d_4^{20} 0.9876; MR_D 78.73; calculated MR_D 78.71. Yield 50%.

Found %: H 7.66; C 79.96; Si 11.07
 $C_{16}H_{18}Si$. Calculated %: H 7.62; C 80.62; Si 11.77.

Allyltrimethylsilane $(CH_3)_3SiCH_2CH=CH_2$ (III). This product has been described by Sommer [9]. Me_3SiAl was, similarly to $PhMe_2SiAl$, prepared by Yavorsky's method. The use of this method is not only simpler, but it also gives higher yields, which are 8% greater than those obtained by the method involving separate preparation of $AlMgX$. Allyltrimethylsilane has b.p. $85.4^\circ/750$ mm; n_D^{20} 1.4075; d_4^{20} 0.7195. Yield 59%.

Allyltripropylsilane $(CH_3CH_2CH_2)_3SiCH_2CH=CH_2$ (IV); b.p. $217^\circ/748$ mm; n_D^{20} 1.4490; d_4^{20} 0.7950; MR_D 65.93; calculated MR_D 66.85. Yield 51%.

Found %: H 13.28; C 72.28; Si 13.83
 $C_{12}H_{20}Si$. Calculated %: H 13.21; C 72.64; Si 14.14

Allyltributylsilane $(CH_3CH_2CH_2CH_2)_3SiCH_2CH=CH_2$ (V). This has been described by Petrov and Shchukovsky; it has b.p. $252.3^\circ/750$ mm; n_D^{20} 1.4515.

Triallylpropylsilane $CH_3CH_2CH_2Si(CH_2CH=CH_2)_3$ (VI); b.p. $218.3^\circ/750$ mm; n_D^{20} 1.4705; d_4^{20} 0.8178; MR_D 66.37; calculated MR_D 65.91. Yield 36.6%.

Found %: H 11.66; C 74.14; Si 13.88
 $C_{12}H_{22}Si$. Calculated %: H 11.41; C 74.15; Si 14.44

Phenyltriallylsilane $C_6H_5Si(CH_2CH=CH_2)_3$ (VII); b.p. 274.8° (751) n_D^{20} 1.5300; d_4^{20} 0.9174; MR_D 76.90; calculated MR_D 76.47.

Found %: H 9.14; C 78.95
 $C_{15}H_{20}Si$. Calculated %: H 8.83; C 78.88

β -Bromopropyltrialkylsilanes $R_3SiCH_2CH(CH_2)Br$. These were obtained in the usual way [6] by bubbling HBr through compounds (I), (II), (III), (IV), and (V) at -70° . The β -bromides obtained from compounds I and V were very viscous oils. The β -bromides were not purified, but were taken directly for the reactions; the β -chloride obtained from compound (II) and HCl was, however, first purified.

β -Chloropropyltrimethylsilane $(CH_3)_3SiCH_2CH(CH_2)Cl$ (VIII); b.p. $43-46^\circ/25$ mm; n_D^{20} 1.4280; d_4^{20} 0.8738; MR_D 44.37; calculated MR_D 44.38.

Found %: Cl 23.64
 $C_6H_{15}SiCl$. Calculated %: Cl 23.53

β -Alkylpropyltrialkylsilanes (trialkyl-2-methylalkylsilanes) $R_3SiCH_2CH(R)CH_3$



The β -bromides were added to a 2-3 fold excess of $R'MgX$, which was prepared in the usual way from the appropriate $R'X$ and Mg ; the amount of β -bromide taken varied from 0.15 to 0.3 moles, and it was added at -70° . The reaction with allyl bromide was conducted according to Yavorsky, and it was possible, during the addition of β -bromide to $R'MgX$, to estimate the extent of β -decomposition from the amount of propylene evolved. After adding the β -bromide the mixture was boiled for 5-8 hrs, after which the ether was in some cases distilled off and the solid residue was heated on a boiling water bath, in order to convert the β -decomposition product R_3SiBr into R_3SiR' . Otherwise, during the subsequent decomposition with water, formation of the corresponding silanols R_3SiOH and disiloxans $R_3SiOSiR_3$ takes place, and these products interfere with the purification of the main product. After treatment with water, drying, and distilling off the ether, the residue is fractionally distilled. In preparing saturated silicohydrocarbons the residue was first extracted with concentrated sulfuric acid. The yields and properties of the products are presented in Tables 1 and 2.

The new silicohydrocarbons Pr_3SiEt and Bu_3SiEt were obtained incidentally to the preparation of compounds (7) and (10). The corresponding R_3SiR' or R_3SiOH and $R_3SiOSiR_3$ compounds were formed as a result of β -decomposition in the other cases, except for compounds (8), (9), and (13), where there was apparently no β -decomposition.

Ethyltripropylsilane $(CH_3CH_2CH_2)_3SiC_2H_5$ (IX): b.p. 207-210° (748); n_D^{20} 1.4375; d_4^{20} 0.7824; MR_D 62.47; calculated MR_D 62.69.

Found %: H 13.98; C 70.32; Si 14.66
 $C_{11}H_{24}Si$. Calculated %: H 14.06; C 70.88; Si 15.06

Ethyltributylsilane $(CH_3CH_2CH_2CH_2)_3SiC_2H_5$ (X): b.p. 252-254° (740); n_D^{20} 1.4445; d_4^{20} 0.7942; MR_D 76.49; calculated MR_D 76.58.

Found %: Si 12.22
 $C_{14}H_{30}Si$. Calculated %: Si 12.28

1,4-Di-(trimethylsilyl)-2,3-dimethylbutane $(CH_3)_3SiCH_2CH(CH_3)CH_2Si(CH_3)_3$ (XI)



Compound (III) and HBr give 71.5 g (0.366 moles) of trimethyl- β -bromopropylsilane, a few ml of which is added to 20 g (0.824 moles) of magnesium powder in 250 ml of ether, contained in a 500 ml flask. A violent exothermic reaction at once begins, and the mixture becomes black. The β -bromide is added during 90 min., with energetic stirring, and maintaining the temperature at $10-15^\circ$ (evolution of gas is considerable at $20-25^\circ$, and at the b.p. of ether the yields of silicohydrocarbons are less than a half of those at $10-15^\circ$). The contents of the flask are treated with water on the following day, the ethereal layer is separated, and the ether is distilled off. The residue is treated with concentrated sulfuric acid, and the acid layer is poured into water, when hexamethyldisiloxane separates. The product not extracted by sulfuric acid is washed with water, dried, and fractionally distilled, to yield 3.2 g of trimethylpropylsilane [10] b.p. $88^\circ/736$ mm; n_D^{20} 1.3929; d_4^{20} 0.7027 and 5.2 g of a substance of b.p. $218-220.5^\circ$; this was 1,4-di-(trimethylsilyl)-2,3-dimethylbutane, b.p. $220-220.3^\circ/730$ mm; n_D^{20} 1.4400; d_4^{20} 0.7922; MR_D 76.68; calculated MR_D 76.95. Yield 12.3%.

Found %: H 13.04; C 62.69; Si 23.48
 $C_{12}H_{26}Si_2$. Calculated %: H 13.12; C 62.53; Si 24.35

Trimethyl-4-bromo-2-methylpentylsilane (δ -bromide) $(CH_3)_3SiCH_2CHCH_2CHBr$ (XII)



HBr is passed through 18.7 g (0.17 moles) of trimethyl-2-methylbut-3-enylsilane (see Table 2), cooling in a freezing mixture containing dry ice, and continuing the reaction until the theoretical gain in weight is achieved. The temperature of the mixture is then allowed to rise to room temperature, when considerable amounts of HBr are evolved; the product is for this reason again cooled and saturated with HBr at -70° , and this treatment is repeated until the gain in weight at 20° corresponds with the theoretical. Fractionation of the product gave 25.5 g of trimethyl-4-bromo-2-methylpentylsilane, b.p. $92-93^\circ/18$ mm; n_D^{20} 1.4590; d_4^{20} 1.0628; MR_D 61.02; calculated MR_D 61.11. Yield 90%.

TABLE 2

New silicohydrocarbons of the type $R_3Si-C-C-R'$

No.	Formula	R	R'	B.p. °C	D mm.	n_D^{20}	d_4^{20}	MR _D found	MR _D calc.	M	Calculated %			Found %		
											C	H	Si	C	H	Si
1	$C_{13}H_{22}Si$	PhMe ₂	Et	242	735	1.4895	0.8806	67.70	68.62	203.37	75.66	10.75	13.60	—	—	13.4
2	$C_{14}H_{22}Si$	PhMe ₂	Al	250-8	743	1.4990	0.8859	72.38	72.00	218.38	76.99	10.15	12.85	—	—	12.21
3	$C_{15}H_{22}Si$	Me ₂	Et	133.2	747	1.4120	0.7369	48.72	48.80	144.3	66.58	13.97	19.45	66.41	13.96	19.20
4	$C_{15}H_{22}Si$	—	Pr	154.5	750	1.4190	0.7492	53.37	53.43	158.33	68.27	14.01	17.72	68.58	14.02	—
5	$C_{15}H_{22}Si$	—	Ph	221-3	745	1.4940	0.8792	63.69	63.78	192.34	74.93	10.48	14.59	75.70	10.37	13.75
6	$C_{15}H_{22}Si$	—	Al	151.3	750	1.4264	0.7575	52.91	52.96	156.31	69.15	12.90	17.95	69.18	12.82	—
7	$C_{14}H_{22}Si$	Pr ₂	Et	240-3	745	1.4450	0.7965	76.54	76.58	228.46	73.60	14.12	12.28	73.64	14.00	12.42
8	$C_{15}H_{22}Si$	—	Pr	257-9	750	1.4470	0.8011	80.87	81.21	242.48	74.29	14.13	11.57	74.50	14.14	11.21
9	$C_{15}H_{22}Si$	—	Al	255-6	760	1.4545	0.8098	80.49	80.74	240.47	74.92	13.41	11.67	74.99	13.10	—
10	$C_{17}H_{22}Si$	Bu ₂	Et	272-4	740	1.4480	0.8010	90.41	90.47	270.53	75.47	14.16	10.37	—	—	10.99
11	$C_{15}H_{22}Si$	—	Al	288-9	745	1.4568	0.8122	94.70	94.84	282.54	76.51	13.56	9.93	76.60	13.69	9.56

Triethyl-4-bromo-2-methylpentylsilane $(C_2H_5)_3SiCH_2CHCH_2CHBr$ (XIII)

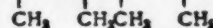
This was prepared similarly to the preceding δ -bromide from triethyl-2-methylbut-3-enylsilane [6], and had b.p. 124°/8 mm., n_D^{20} 1.4745; d_4^{20} 1.0517; MR_D 74.70; calculated MR_D 75.00. Yield 84%.

6-Trimethylsilyl-3,5-dimethylhexanol $(CH_3)_3SiCH_2CHCH_2CHCH_2CH_2OH$ (XIV)

The Grignard reagent was prepared from 22 g of the δ -bromide (XI) (0.093 moles) and 2.5 g of magnesium (0.103 moles) in 100 ml of ether; the reaction proceeds energetically, and after its completion the mixture is boiled for 2 hours, after which 11 g of ethylene oxide (0.25 moles) and 150 ml of ether are added. The contents of the flask, which had set to a jelly by the next day, were left for 8 days, and were then treated with water. Fractional distillation of the dried ethereal layer gave 7 g of the alcohol (XIV), b.p. 120-125°/5 mm., n_D^{20} 1.4480; d_4^{20} 0.8315; MR_D 65.16; calculated MR_D 64.24. Yield 37.2%.

Found %: Si 14.78; 15.31. $C_{11}H_{22}SiO$. Calculated %: Si 13.87.

The results both of elementary analysis and of OH group determination by Tseretvintov's method (83%) suggested contamination of the product with a silicohydrocarbon, and a substance which was insoluble in concentrated H_2SO_4 , b.p. about 300°, n_D^{20} 1.4510, was found in the higher b.p. fractions. We considered this to be a silicohydrocarbon produced by a Wurtz condensation of the δ -bromide, as in the case of reaction (XI) for the δ -bromide. This supposition was confirmed by the results of the next experiment.

1,8-Di-(triethylsilyl)-2,4,5,7-tetramethyloctane $(C_2H_5)_3SiCH_2CHCH_2CHCH_2CHCH_2CHCH_2Si(C_2H_5)_3$ (XV)

18 g of the δ -bromide (XIII) (0.066 moles) is added to 1.6 g of Mg powder (0.066 moles) in 50 ml of ether. After completion of the reaction, initiated by addition of a crystal of iodine, the reaction mixture is boiled for 5 hours, and is then treated with water and 10% HCl. The ether is distilled off, and the residue is treated with concentrated H_2SO_4 . The residue insoluble in H_2SO_4 consists of 3 g of triethyl-2-methylpentylsilane [6], b.p. 222-226°, n_D^{20} 1.4436, and 7 g of compound (XV), b.p. about 380°, n_D^{20} 1.4687; d_4^{20} 0.8443; MR_D 131.5; calculated MR_D 132.4.

Found %: H 13.64; C 72.62; Si 13.69; $C_{22}H_{44}Si_2$. Calculated %: H 13.65; C 72.27; Si 14.08.

The fraction soluble in H_2SO_4 was recovered by pouring the solution into water; it consists of about 1 g of hexaethyldisiloxane, and about 2 g of higher b.p. fractions.

The analyses were performed in the Microanalysis Laboratory, Institute of Organic Chemistry, Academy of Sciences U.S.S.R.

SUMMARY

1. Contrary to the views of American workers, it has been shown that β -silylalkyl halides may be used for the synthesis of silicohydrocarbons by the Grignard-Wurtz reaction; this is illustrated by the synthesis of 12

silicohydrocarbons, in yields of 20-50% (not counting a large number of syntheses with smaller yields).

2. A mechanism is advanced for the so-called β -decomposition of β -silicoalkyl halides ($R_3Si-C-C-X$). This consists of liberation of an olefin molecule, with attachment of the β -halogen atom to the silicon. The reaction may proceed spontaneously, at temperatures of from $+50^\circ$ to -50° , according to the structure of the silicoalkyl halide, or it may be activated by the Grignard reagents. The Grignard reagents $R'MgX$ react simultaneously both with the product of β -decomposition R_3SiX and with the β -silicoalkyl halides, the yields of silicohydrocarbons (products of β -decomposition or of synthesis) varying widely according to the nature of R and R' .

3. It is shown that the amount of β -decomposition falls in the series primary \rightarrow secondary \rightarrow tertiary silicoalkyl halides, and is greater for bromides than for chlorides. The radical R also affects the results, the yield of decomposition products falling, and of synthesis products rising, in the order C_6H_5 , CH_3 , C_2H_5 , C_3H_7 , C_4H_9 , i.e., in order of diminishing electronegativity of the radicals. The extent of β -decomposition could in some cases be reduced by conducting the syntheses at low temperature.

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Institute of Organic Chemistry, Academy of Sciences U.S.S.R.
D. I. Mendeleev Moscow Institute for Chemical Technology

CATALYTIC ALKYLATION OF AMMONIA WITH HALOGEN DERIVATIVES OF ALKANES AND CYCLANES

PART 2. EFFECT OF THE NATURE OF THE HALOGEN AND OF ITS POSITION IN THE MOLECULE ON AMINATION OF ALKYL HALIDES

V. A. Nekrasova and N. I. Shul'kin

We know from the literature of the problem of amination of alkyl halides [1] that the most suitable for liquid phase amination are chloro- and bromo-derivatives. We thought it of interest to investigate the behavior of halides of aliphatic and alicyclic hydrocarbons in conditions of catalytic amination in the vapor phase.

Our experiments showed that the nature of the halogen, and its position in the chain significantly affect the results. We made a comparative study of amination of chloro-, bromo-, and iodo-ethane, 1-chloro-2-methylpropane, 1-bromo-2-methylpropane, 1-chlorooctane, and 1-bromooctane, at a catalyst based on magnesium oxide. The volume of catalyst was in all cases 100 ml, and the molecular ratio of ammonia to organic halide was 2:1. The experiments lasted 1 hour, at 310°, at a rate of flow of 0.2 (volume velocity). The properties of the halides taken are given in Table 1, and the experimental results are presented in Table 2.

TABLE 1
Properties of the Alkyl Halides Taken

Alkyl halide	B.P. °C (corr.)	n_D^{20}	d_4^{20}
Chloroethane	12.5	—	0.9170 (d_4^{20})
Bromoethane	38.5 (753 mm)	1.4238	1.4553
Iodoethane	72.5	1.5168	1.9132 (d_4^{20})
1-Chlorobutane	78.5	1.4015	0.8840
1-Bromobutane	101.0	1.4358	1.2689
1-Iodobutane	131.0	1.5060	1.6160
1-Chlorooctane	184.0	1.4425	0.8969
1-Bromooctane	201.5	1.4525	1.1078

The experiments showed that variations in the position of the halogen atom have a considerable effect on the yields, but that isomerism of the hydrocarbon chain was practically without effect; the results for 1-chlorobutane, 1-chloro-2-methylpropane, 2-chlorobutane, 2-chloro-2-methylpropane, 1-chlorohexane, 2-chlorohexane, 1-chloropentane, 2-chloropentane, 1-chlorooctane, and 2-chlorooctane are given in Tables 2 and 3. Primary chloroalkanes give a higher yield of amines than do secondary ones; thus the catalyzate from 1-chlorobutane contains 11.4 % of amino-nitrogen, as compared with only 8.6% from 2-chlorobutane. Comparison of amination

of 1-chlorobutane and 1-chloro-2-methylpropane shows that isomerism of the hydrocarbon chain has little effect, the amino-nitrogen contents of the catalyzates being 11.4 and 10.9% respectively.

TABLE 2
Dependence of Yield of Amines on the Nature of the Halogen

Alkyl halide	Yield of condensate, as % of initial alkyl halide	% Amino-nitrogen content of catalyzate
Chloroethane	85.0	12.9
Bromoethane	80.0	9.9
Iodoethane	32.9	6.7
1-Chlorobutane	85.2	11.4
1-Bromobutane	78.8	9.5
1-Iodobutane	35.4	4.9
1-Chlorooctane	85.1	10.5
1-Bromooctane	80.3	9.1

We next studied vapor phase amination of alicyclic halides, at 340°, other conditions being as above. The results, given in Table 4, show that the same effects are found as for alkanes. The amino-nitrogen content of the catalyzates from chloro- and bromo-cyclohexane is 11.9 and 10.7% respectively.

SUMMARY

1. The conditions for vapor phase contact catalytic amination of halogen derivatives of aliphatic and alicyclic hydrocarbons have been studied.

TABLE 3
Dependence of Yield of Amines on the Position of the Halogen in the Molecule

Chloroalkane	Yield of condensate, as % of initial alkane chloride	% Amino-nitrogen content of the catalyzate
1-Chlorobutane	86.6	11.4
1-Chloro-2-methylpropane	80.1	10.9
2-Chlorobutane	79.2	8.6
2-Chloro-2-methylpropane	78.7	5.6
1-Chlorohexane	82.1	12.0
2-Chlorohexane	79.1	10.1
1-Chloropentane	84.1	11.8
2-Chloropentane	79.2	9.1
1-Chlorooctane	83.2	10.5
2-Chlorooctane	80.1	9.1

TABLE 4
Synthesis of alicyclic amines in the vapor phase, as a magnesium oxide catalyst

Halogen derivative	Yield of condensate, as % of initial halogen derivative	% Amino-nitrogen content of the catalyzate
Chlorocyclopentane	98.1	11.5
Chlorocyclohexane	97.7	11.9
Bromocyclohexane	97.5	10.7

2. The nature of the halogen significantly affects the yields obtained which are higher for chloro- than for bromo-derivatives, and are lowest for iodo-derivatives.

3. The position of the halogen atom in the hydrocarbon chains significantly affects the yields, which are highest for primary alkyl halides.

4. Chlorine derivatives of alicyclic hydrocarbons give higher yields of amines than do bromine derivatives.

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Institute of Organic Chemistry
Academy of Sciences U.S.S.R.

ROLE OF OXYGEN-CONTAINING COMPOUNDS IN THE SYNTHESIS OF HYDROCARBONS FROM CARBON MONOXIDE AND HYDROGEN

Yu. B. Kagan, Yu. B. Krut'kov, E. V. Kamzolnikova, and A. N. Bashkirev

INTRODUCTION

It is generally known that the products of synthesis of hydrocarbons from carbon monoxide and hydrogen, discovered by Orlov [1], always contain a small amount of oxygen-containing organic compounds. This has given rise to the hypothesis [2] that oxygen-containing substances are intermediates in the synthesis of hydrocarbons; this view has had the support of a number of workers [3,4], but has had no further experimental confirmation. Eidus [5] studied the behavior of some of the simplest oxygen-containing compounds (formic acid, methanol, and ethanol) at Co catalysts of synthesis of hydrocarbons at 180-200°, at atmospheric pressure. He found that hydrocarbon synthesis is inhibited by addition of the oxygen-containing substances, showing that they cannot be regarded as intermediates in this synthesis.

New experimental material has, however, recently afforded fresh support for the hypothesis of intermediate formation of oxygen-containing products. In particular, the possibility of achieving synthesis of alcohols and hydrocarbons at one and the same low catalyst at different temperatures has been demonstrated [6]. The chief products of the reaction at low temperatures (190-200°) are alcohols, while at high temperatures (320-330°) the products are hydrocarbons. Storch [6] hence concludes that alcohols should be regarded as intermediate products in the synthesis of hydrocarbons, obtained therefrom by dehydration. Hall [7] attempted to confirm this view experimentally, and showed that with six-fold increase of velocity of flow of the gas the alcohol content of the product rises from 1.1 to 1.8% and that lowering of the reaction temperature at a cobalt catalyst also leads to increase in the yield of alcohols. This author [7] further studied the behavior of n-propanol and n-octanol at the catalysts Co-ThO₂-MgO-kieselguhr (100:6:3:200) and Fe-Cu-CaO-kieselguhr (100:5:10:30) in a stream of hydrogen, nitrogen and water gas, at the temperatures of the synthesis.

The author found that the amounts of unreacted alcohols varied, from 0 to 72% but, as the author himself admits [7], the products were not studied sufficiently. All that we know of them is that "on the basis of preliminary studies the chief products obtained at 150° appear to be water and the corresponding olefin and paraffin". Apart from these, propanol, at the same temperature, gave a liquid product of high b.p., which was not further examined, and octanol, at higher temperatures (183°), gave gaseous hydrocarbons and liquid products which boiled over a wide range of temperatures. Hall [7] draws the conclusion from these results that dehydration of the alcohols takes place, with production of olefin and for this reason he considers that alcohols may be intermediate products in the synthesis of hydrocarbons.

It seems to us, however, that these experimental results do not support such a view of the mechanism of the reaction. It should be stressed, in the first place, that it is impossible to draw conclusions regarding the nature and direction of the processes taking place unless we know the composition of the products obtained. It is also significant that when the experiments were performed under the conditions of the synthesis of hydrocarbons (in a stream of CO + H₂) the least conversion of alcohols was obtained. This fact is not in accord with the view that alcohols are intermediate products in the process of synthesis of hydrocarbons.

The results obtained by Hall in a single experiment involving variation in the rate of flow are also not conclusive, firstly because the absolute amount of alcohols in the reaction products is small, and secondly because with increase in the rate of flow the increase in the yield of alcohols is paralleled by increase in the yield of olefins. The experimental material presented below was obtained by us in connection with the study of the behavior of certain alcohols under the conditions of synthesis of hydrocarbons from carbon monoxide and hydrogen; it is in contradiction to Hall's view that hydrocarbons are formed from intermediate oxygen-containing compounds.

EXPERIMENTAL

The experiments were conducted in continuous action apparatus, working under pressure. The reactor in which the catalyst was placed was a steel tube, embedded in an aluminum block, the internal diameter of the tube being 14 mm. Our earlier papers [8, 9] give a description of the apparatus and method applied, and of the way in which the experimental data were evaluated. The apparatus was provided with a dropper, placed between the meter registering rate of flow of gas for synthesis and the reactor. A system of valves permitted the dropper to be included in the system without interrupting the reaction. An iron-containing catalyst was used. The initial gas contained carbon monoxide and hydrogen, in the proportion 1:1. The temperature applied was 300°, and the pressure was 20 atm.

BEHAVIOR OF n-BUTANOL UNDER SYNTHESIS CONDITIONS

n-Butanol, b.p. 117.3-117.8°, n_D^{20} 1.3991; d_4^{20} 0.8103, was introduced into the stream of CO-H by means of the dropping funnel. It had been shown previously that the catalyst is highly active, and that synthesis of hydrocarbons proceeds normally, with practically complete conversion of the carbon monoxide. The experiment lasted for 6 hours, during which time 34.5 g of n-butanol was added, and 32.5 g of liquid products were collected, together with 0.5 ml of gasoline vapor and 700 ml of "Gasol" in the absorber. Synthesis of hydrocarbons continued under the given conditions, although at a much slower rate.

The hydroxyl number of the condensate was 232, the ester number 138, and the acid number 4. The liquid reaction products (25.36 g) were subjected to detailed examination; the results of fractional distillation and analysis are presented in Table 1.

TABLE 1
Results of Fractional Distillation and of Analysis of the Product
Obtained when n-Butanol is Added to the Synthesis Gas Mixture

B.p. of fraction, °C	Weight of fraction, g	% content of aldehydes	Weight of aldehydes, g	Acid number	Weight of acids, g	Hydroxyl number	Wt. of alcohols, g	Ester number	Weight of esters, g
40-60	0.45	—	—	—	—	—	—	—	—
60-80	1.40	6.7	0.09	0	0	—	—	—	—
80-110	7.17	9.2	0.66	0	0	260	2.46	0	0
110-125	5.46	1.6	0.09	0	0	670	4.83	41.9	0.59
125-158	1.95	0	0	5.25	0.016	345	0.89	210	1.05
158-168	7.36	0	0	7.1	0.080	0	0	379	7.18
Residue and losses	1.57	—	—	—	—	—	—	—	—
Weight of product	25.36	3.3	0.84	—	0.096	—	8.18	—	8.82

NOTE: The amount of oxygenous compounds was calculated on the basis of the data cited below.

The data of Table 1 show that the product obtained is clearly not homogenous. Its fractional composition, the distribution of the ester numbers among the fractions, and, in particular, the very high ester number of the fraction of b.p. 158-168°, show that the product consists basically of esters. A certain amount of acids are also formed, mostly in the fraction boiling at 158-168°, and of aldehydes, concentrated mostly in the fraction boiling at 80-110°.

The distribution of hydroxyl numbers through all the fractions suggests that the alcohol present in the catalyzate is unreacted n-butanol. The structure of the ester and aldehyde obtained were the subject of a special study.

STRUCTURE OF THE ESTER

Acids were eliminated from the fraction of b.p. 158-168°, and the residue was distilled, collecting the fraction of b.p. 165-167° (2.92 g). The constants of the fraction are given in Table 2.

The comparison of constants suggests that the ester is n-butyl n-butyrate.

TABLE 2
Constants of the Fraction of b.p. 165-167°

	Boiling point, °C	d_4^{20}	n_D^{20}	Ester number
Found	165-167	0.8694	1.4088	387.5
Published values for n-butyl n-butyrate [10]	166.4	0.872	1.4049	388.7

The whole of the fraction of b.p. 158-168° was hydrolyzed, and the resulting alcohol (1 g), b.p. 116-118°, d_4^{20} 0.8109; n_D^{20} 1.3984, was collected. The m.p. of the phenylurethane prepared therefrom, and recrystallized from petroleum ether, was 60°, and it did not give any depression with the phenylurethane of n-butanol. According to the literature, n-butanol has b.p. 117.7°, d_4^{20} 0.810; n_D^{20} 1.3993 [11], m.p. of phenylurethane 61°. The alcohol derived from hydrolysis of the ester is thus definitely shown to be n-butanol.

The salt of the organic acid present in the alkaline hydrolyzate was decomposed with 15% H_2SO_4 , and the solution was extracted with ether, giving 2.5 g of a product boiling at 162-163.5°, which is the b.p. of n-butyric acid. The acid was definitely identified from its physical constants and acid number, and from the m.p. of its amide and the results of analysis of its silver salt.

TABLE 3
Constants of the Acid Obtained by Hydrolysis of the Fraction of b.p. 158-168°

	Boiling point, °C	d_4^{20}	n_D^{20}	Acid number	Melting point of amide, °C
Found	162-163.2	0.9564	1.3982	616.2	114.5-115
Published values for n-butyric acid [10]	163.5	0.9590	1.3979	636.5	115

The amide gave no m.p. depression with n-butyramide. The silver content of the silver salt of the acid was determined.

Found %: Ag 55.48.
 $C_4H_7O_2Ag$ Calculated %
Ag 55.34.

The ester was thus definitely identified as n-butyl n-butyrate.

IDENTIFICATION OF THE ALDEHYDE

A hydrochloric acid solution of 2:4-dinitrophenylhydrazine was added to the fraction of b.p. 80-110°, to give the 2:4-dinitrophenylhydrazone of the aldehyde contained in this fraction; after recrystallization from ethanol it melted at 121-122°. According to the literature [13] the m.p. of the 2:4-dinitrophenylhydrazone of n-butyraldehyde is 122°. The mixed m.p. shows no depression. It may hence be accepted that the aldehyde obtained is n-butyraldehyde.

The elucidation of the structure of the reaction products allows of their determination in the catalyzate (see Table 1). From the above values for hydroxyl, acid, and ester numbers, together with other data from Table 1, we obtain the following reaction balances:

n-Butanol introduced into the reaction	34.5 g
Found in the catalyzate:	
n-Butanol	10.60 g
Butyl butyrate, n-butyraldehyde, and n-butyric acid	12.63 g
Other liquid and gaseous products	10.67 g
Total	33.90 g

It is evident from this balance that of 34.5 g of n-butanol taken in the reaction 23.2 g was found in the catalyzate in the form of unreacted alcohol and of its oxygenous conversion products. Even if we assume that the whole of the remaining n-butanol has undergone conversion into hydrocarbons it is evident that oxygen-containing products are greatly in excess of hydrocarbon products. It would follow that if n-butanol is an intermediate product in the synthesis of hydrocarbons from carbon monoxide and hydrogen we should expect to find an excess of oxygen-containing products in the catalyzate: this, however, is in contradiction to all the known experimental facts relating to the product of synthesis at an iron-containing catalyst under the given experimental conditions. This shows, therefore, that n-butanol cannot be regarded as an intermediate product of the synthesis of hydrocarbons from carbon monoxide and hydrogen.

The behavior of n-butanol was also studied under conditions of synthesis of hydrocarbons at atmospheric

pressure. We used a typical alkali-activated precipitated iron-copper catalyst. The experiments were performed at 240°, using 1:1 CO-H₂ mixtures, passed through the catalyst at a volume velocity of about 100 hr⁻¹. The gas mixture contained, apart from the carbon monoxide and hydrogen, about 3% of n-butanol vapor. The fractional composition and the analytical data for the reaction product are given in Table 4.

TABLE 4

Characterization of the Product Obtained when n-Butanol is added to the Reaction Gas at Atmospheric Pressure

Boiling point of fraction, °C	% Content of fraction in product	Acid number	Hydroxyl number	Ester number	% Content of aldehyde (C ₃ H ₇ O) in the fraction
Up to 100	16.9	—	—	—	35.6
100-130	34.2	1.67	720	30.8	—
130-170	15.3	33.9	182	229.3	0
Solid residue	33.6	—	—	—	—

The values given in Table 4 show that n-butanol undergoes the same conversions under conditions of synthesis at atmospheric pressure as in the earlier experiments at higher pressures.

BEHAVIOR OF N-PROPANOL UNDER CONDITIONS OF SYNTHESIS

n-Propanol, b.p. 96.6–97.0°; d_4^{20} 0.8039; n_D^{20} 1.3853, was introduced into the reactor in the way described above. The catalyst was first tested for 10 days with only CO-H₂ mixture, at 300°/20 atm., and was found to be highly active. The productivity of the whole of the catalyst volume, with a rate of flow of the gas of 30 l. per hour, was about 4 g of hydrocarbon per hour, with 90% conversion of the carbon monoxide. In experiments with n-propanol the alcohol was added at a rate approximately equal to that of production of hydrocarbon, as found in the preliminary experiments, but the rate of delivery of the gas was reduced to a third, so that a considerable part of the catalyst surface remained free.

TABLE 5

Rate of supply of gas for synthesis, in l./hr.	% Contraction	% Conversion	Yield of hydrocarbons, ml/hr	
			Liquid	Gaseous
10	59	89.4	0.98	310

At this reduced rate of delivery of the initial gas hydrocarbon synthesis (before addition of propanol) was as shown in Table 5.

27 g of propanol was placed in the dropping funnel, and was delivered to the reactor during 9.5 hour. This gave 34.26 g of liquid products, and 4000 ml of gaseous hydrocarbons, i.e., 1100 ml more than is obtained during the

same time under ordinary conditions. The percentage composition of the initial gas and of that obtained from it 4.5 hours after addition of alcohol were as follows:

Gas	CO ₂	C _n H _m	CO	H ₂	CH ₄
Initial	—	—	47.0	53.0	—
Final	43.3	5.7	4.3	43.2	3.6

Applying the formula proposed by certain of us [9] for the calculation of contraction:

$$K = \frac{3a_1 + 2b_1 - c_1 - d_1}{3a_2 + 2b_2 - c_2 - d_2}$$

where a_1 , b_1 , c_1 and d_1 are the CO₂, CO, H₂ and CH₄ contents of the gas initially and a_2 , b_2 , c_2 and d_2 are the corresponding values in the issuing gas, we find a value for contraction of 57.6% (experimental value 59.0%).

Applying the method of calculation earlier described [9], we obtain the following reaction balances:

1 cu. m. of the initial gas contains	470 l CO + 530 l H ₂	Expressed gravimetrically:	gC	gH	gO
0.424 cu. m. of the final gas contains	19 l CO + 194 l H ₂				
Total entering into reaction	451 l CO + 336 l H ₂	The reacted gas contains	242.0	30.0	322.2
Of the reacted gas:		The CO ₂ obtained contains	104.0	—	278.0
Converted into CO ₂	194 l CO	The H ₂ O obtained contains	—	5.6	45.0
Converted into H ₂ O		The CH ₄ obtained contains	8.6	2.9	—
Converted into CH ₄	16 l CO	The higher hydrocarbons obtained contain	129.0	21.5	—
Converted into higher hydrocarbons (C _n H _m)	241 l CO	The reaction products obtained contain	241.6	30.0	323.0

As is evident from these values, the synthesis of hydrocarbons proceeds with the same speed when n-propanol is introduced, and the degree of conversion of CO achieves 96%.

The liquid reaction products were next examined. The liquid was fractionated, and the aldehyde content and hydroxyl, acid, and ester numbers were determined for each fraction (see Table 6).

The calculation of the content of oxygen-containing compounds is based on the assumption that the process of conversion of n-propanol proceeds analogously to that of n-butanol. The data of Table 6 show that the amount of unreacted alcohol exceeds 50%. The total amount of oxygen-containing products of conversion of n-propanol is at least 4.4 g., and of liquid hydrocarbons not more than 10-11 g.

Under the given conditions, synthesis from carbon monoxide and hydrogen should during 9.5 hr. have given rise to about 7 g of liquid and at least 2000 ml of gaseous hydrocarbons (see Table 5). Even if we assume that all the remaining liquid and gaseous hydrocarbon products of the reaction resulted from conversion of n-propanol, the amount of hydrocarbons so formed would be approximately equal to that of oxygen-containing products actually obtained from n-propanol.

TABLE 6
Characterization of the Products Obtained when n-Propanol is added to the Reaction Gas

Boiling point of fraction, °C	Weight of fraction, g	% Content of aldehydes	Aldehyde content, g	Hydroxyl number	Alcohol content, g	Acid number	Content of acids, g	Ester number	Ester content, g
45-70	1.4	26.5	0.37	—	—	—	—	—	—
70-95	19.65	6.5	1.30	532	11.20	0.5	—	50.5	2.04
95-150	2.5	—	—	665	1.77	40.0	0.13	75	0.39
Residue	3.5	—	—	—	—	—	—	—	—
Losses	4.2	—	—	—	—	—	—	—	—
Reaction	3.0	3.6	0.11	200	0.64	—	—	—	—
For the whole of the product	34.25	—	1.78	—	13.61	—	0.13	—	2.43

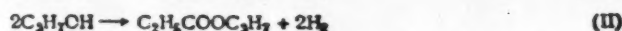
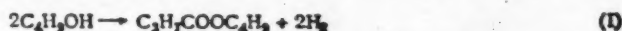
Note: Fractional distillation was conducted from a Favorsky flask.

that n-propanol can also not be regarded as an intermediate product in the synthesis of hydrocarbons from carbon monoxide and hydrogen.

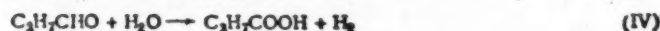
This fact, and also the relatively low degree of conversion of alcohol under conditions in which a considerable part of the synthetically active surface remains unoccupied, and in which practically total conversion of carbon monoxide takes place, show

DISCUSSION OF THE RESULTS OBTAINED

The experimental material presented above showed that neither n-butanol nor n-propanol can be considered as intermediate products in the synthesis of hydrocarbons. These researches showed, moreover, that at the iron catalyst, under the given conditions, an ester-producing condensation of n-butanol and n-propanol takes place.



This condensation has been investigated in detail by numerous authors. The following mechanism seems, from a study of the literature [14, 15, 16], to be the most probable. It involved the three successive processes



The composition of the reaction product obtained in our experiments agrees well with this scheme [equations (III), (IV) and (V)].

It is significant that of these conversions the first two, (III) and (IV) are oxidation reactions, the oxidizing agent in reaction (IV) being water. This is of particular interest in view of our earlier finding [8, 17, 18] that the iron catalysts are able, under conditions of hydrocarbon synthesis from carbon monoxide and hydrogen, to catalyze the reaction of oxidation of carbon monoxide with steam, suggesting that these catalysts may have the general property of accelerating reactions of oxidation by water.

Their catalytic powers are not, however, limited to these reactions. Equation (III) points to the dehydrogenating activity of these catalysts under conditions of hydrocarbon synthesis. The property, reported in this and in earlier papers [8, 17, 18], of iron catalysts of hydrocarbon synthesis to accelerate different oxidation reactions should be regarded as one of their most important properties, emerging from the insoluble unity of reactions of oxidation and reduction.

From this viewpoint it seems quite probable that the various oxygen-containing by-products of the process of synthesis of hydrocarbons are formed as a result of oxidation-reduction reactions of any oxygen-containing synthesis products, which are primary products in relation to other oxygen-containing products. Such a primary product of the side-reaction might, for example, be an aldehyde, formed from the appropriate olefin and $\text{CO} + \text{H}_2$. Objections to such a mechanism might be based on the widely held view [7] that such reactions are not promoted by iron catalysts, and that the result of such reactions should be the formation in approximately equal amount of n- and iso-aldehydes and alcohols.

A paper has, however, appeared recently [19], reporting that a catalytic reaction may be achieved in the presence of iron carbonyl and isocarbonyl between olefins, carbon monoxide, and hydrogen, leading to formation of normal alcohols, without any admixture of iso-alcohols. This supports the view that the reaction proceeds as we postulate above.

SUMMARY

1. It has been shown that alcohols cannot be considered to be intermediate compounds in the synthesis of hydrocarbons.
2. It has been shown that iron catalysts of the synthesis of hydrocarbons are capable under the conditions of the synthesis reaction of accelerating the reactions of oxidation of alcohols and aldehydes.
3. Hypotheses regarding the possible mechanism of formation of the various oxygen-containing by-products of the reaction of synthesis of hydrocarbons are advanced.

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Petroleum Institute
Academy of Sciences USSR

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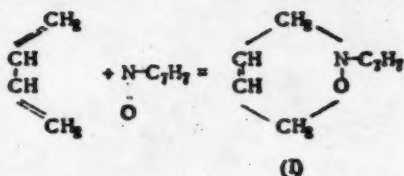
REACTIONS OF DIENE HYDROCARBONS WITH NITROSO-COMPOUNDS

ADDITION OF BUTA-1,3-DIENE TO p-NITROSOTOLUENE

Yu. A. Arbuzov

The results of a study of the reaction of nitrosobenzene with buta-1,3-diene [1,2] showed that addition takes place according to the diene synthesis, with production of 2-phenyl-3,6-dihydro-orthoxazine, the structure of which was derived from a study of the structure of its reduction products.

The results of a study of the reaction of addition of buta-1,3-diene to p-nitrosotoluene, which should lead to formation of 2-p-tolyl-3,6-dihydro-orthoxazine (I), are presented in this paper:

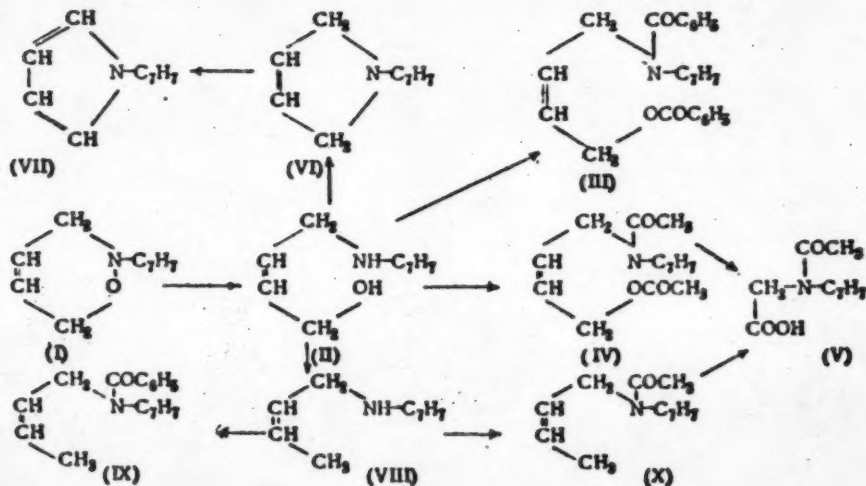


In our first experiment we left a sealed tube containing p-nitrosotoluene and excess of buta-1,3-butadiene in a cold water bath for a day, during which time the color of the solution changed from green to light brown. The tube was then opened, excess of butadiene was evaporated off, and the residue was recrystallized from cyclohexane and then from ethanol, to give colorless needles of the 1:1 addition product, $\text{C}_{11}\text{H}_{13}\text{ON}$, m.p. 46-47°, yield 57% of theory.

The next experiment was conducted at 0°, using organic solvents (chloroform, ether). The flask was removed from the ice bath after 1-2 days, the solvent was evaporated off, and the residue was steam- or vacuum-distilled, giving a yield of 80-90% of addition product.

The addition product was readily soluble in hot cyclohexane, methanol, ethanol, and ether, and in cold glacial acetic acid and chloroform, but is not soluble in water. It can be distilled without decomposition at reduced pressure (b.p. 112-113°/3mm) or with steam. It is shown to be 2-p-tolyl-3,6-dihydro-orthoxazine (I).

Reduction of the addition product with zinc dust in acetic acid gives 4-p-tolylaminobut-2-en-1-ol (II), which gives a crystalline dibenzoyl derivative (III), m.p. 130-131°, and a diacetyl derivative (IV) by the action of acetic anhydride, oxidation of which with potassium permanganate in acetone gives N-acetyl-N-tolylglycine (V).



Reduction of 2-p-tolyl-3,6-dihydro-orthoxazine (I) with zinc dust and acetic acid under more severe conditions gave 1-p-tolyl-2,5-dihdropyrrole (VI), also obtained by heating 4-p-tolylaminobut-2-en-1-ol with zinc chloride in acetic acid. Oxidation of 1-p-tolyl-2,5-dihdropyrrole (VI) with potassium permanganate or ferric chloride gives 1-p-tolylpymole (VII).

Reduction of 2-p-tolyl-3,6-dihydro-orthoxazine (I) with sodium and ethanol or n-butanol gave N-crotyl-p-toluidine (VIII), identified through its benzoyl derivative (IX) and acetyl derivative (X), oxidation of which with potassium permanganate in acetone gave N-acetyl-N-p-tolylglycine (V).

EXPERIMENTAL

Preparation of 2-p-tolyl-3,6-dihydro-orthoxazine

Experiment 1*. 12.1 g (0.1 moles) of p-nitrosotoluene and 21 g of butadiene were placed in a tube cooled in an ethanol-solid carbon dioxide mixture, the tube was sealed, and was immersed in cold water (5-10°) for a day, shaking from time to time during the first 3 hrs. All of the p-nitrosotoluene passed into solution during the first 3.5 hrs. The solution was of a light brown color on the following day, and there were brownish-yellow crystals on the walls of the tube. The tube was cooled and opened, and excess butadiene was allowed to evaporate off. The residue was treated with hot cyclohexane (30 ml), and the solution was filtered hot, leaving a residue of about 0.8 g of a microcrystalline substance. Light yellow crystals separated from the filtrate, and were washed with cyclohexane and then twice recrystallized from 20 ml portions of ethanol, giving 10.0 g of colorless needles, m.p. 46-47°, yield 57% of theory.

Found %: C 75.51; 75.58; H 7.47; 7.44; N 8.18; 8.20
 $C_{11}H_{13}ON$. Calculated %: C 75.40; H 7.48; N 7.99

Experiment 2.** A flask containing 9.6 g (0.08 moles) of p-nitrosotoluene in 75 ml of chloroform was cooled in ice, and 11 g of butadiene was added. The flask was taken out of ice on the next day, and the solvent was distilled off. The residue was steam-distilled, and the crystalline product was recrystallized from methanol, to give 11.3 g of 2-p-tolyl-3,6-dihydro-orthoxazine, m.p. 46-47°, yield 81% of theory.

Experiment 3. 75 g of butadiene was added to a solution of 72.7 g (0.6 moles) of p-nitrosotoluene in 600 ml of chloroform, at 0°, and the solvent was distilled off after 24 hrs at 0°. The residue was vacuum-distilled, to give 94.2 g of 2-p-tolyl-3,6-dihydro-orthoxazine, b.p. 112-113°/3 mm, yield 90%. The product gave colorless needles, m.p. 47-48°, after a single recrystallization from ethanol.

Found %: C 75.40; 75.27; H 7.62; 7.83; N 7.97; 8.02
 $C_{11}H_{13}ON$. Calculated %: C 75.40; H 7.48; N 7.99

Experiment 4. A solution of 30.3 g (0.25 moles) of p-nitrosotoluene and 35 g of butadiene in 500 ml of ether was kept at 0° for 2 days, the ether was distilled off, and the residue steam-distilled. The product separating from the distillate was recrystallized from methanol, giving 35.0 g of colorless needles of 2-p-tolyl-3,6-dihydro-orthoxazine, m.p. 47-48°, yield 80%.

Reduction of 2-p-tolyl-3,6-dihydro-orthoxazine by zinc dust in acetic acid, to give 4-p-tolylaminobut-2-en-1-ol

20 g of zinc dust was added to a solution of 17.5 g (0.1 mole) of 2-p-tolyl-3,6-dihydro-orthoxazine in 200 ml of glacial acetic acid, in a 500 ml bottle, which was corked and shaken vigorously for 10 min. 200 ml of water was added, followed by 275 g of potassium hydroxide, with cooling. The mixture was steam distilled, to remove volatile products, giving 0.5 l. of distillate, and the contents of the distilling flask were filtered hot. The cooled filtrate was extracted with 5 100 ml portions of benzene, the extract was washed with water, the benzene was distilled off, and the residue was fractionally distilled in vacuum, to give 13.8 g of 4-p-tolylaminobut-2-en-1-ol, b.p. 158-159°/3 mm, d_4^{20} 1.0553; n_D^{20} 1.5761; found MR_D 55.57; calculated MR_D 54.06; EMR_D 1.51, yield 78%; a colorless liquid, gradually becoming yellow when kept.

Found %: C 74.40; 74.21; H 8.80; 8.86; N 7.74; 7.72
 $C_{11}H_{15}ON$. Calculated %: C 74.54; H 8.53; N 7.90

- * Experiment performed by the student N. L. Fedyukina.
- ** Experiment performed by the student N. L. Fedyukina.

Dibenzoyl derivative of 4-p-tolylaminobut-2-en-1-ol

5.32 g (0.03 moles) of 4-p-tolylaminobut-2-en-1-ol in 10% sodium hydroxide solution (60 g) is shaken vigorously in a 100 ml bottle with 14.1 g of benzoyl chloride, added in 6 portions during 25 min. Excess of benzoyl chloride is then removed by heating the mixture. The crystalline product is dissolved in ether, and the solution is washed successively with water, 5% caustic soda, 3% hydrochloric acid, and again water. The ether is then distilled off, and the residue is dried in a desiccator over sulfuric acid, giving 11.0 g of ON-dibenzoyl derivative of 4-p-tolylaminobut-2-en-1-ol, m.p. 127.5-130°, yield 95%. The m.p. after two recrystallizations from ethanol is 130-131°.

Found %: C 77.88; 77.88; H 6.02; 6.24; N 3.74; 3.79
 $C_{25}H_{27}O_3N$. Calculated %: C 77.90; H 6.02; N 3.63

Diacetyl derivative of 4-p-tolylaminobut-2-en-1-ol

A solution of 17.7 g (0.1 moles) of 4-p-tolylaminobut-2-en-1-ol in 60 ml of acetic anhydride was heated under reflux on a boiling water bath for 3.5 hrs., after which acetic acid and anhydride were distilled off in vacuum (50 mm), and the residue at 2 mm, to give 23.4 g of the diacetyl derivative of 4-p-tolylaminobut-2-en-1-ol, a colorless viscid liquid, b.p. 167-168°/2 mm, d_4^{25} 1.0855; n_D^{25} 1.5260; found MR_D 73.89; calculated MR_D 72.66; EMR_D 1.23. Yield 90%.

Found %: C 68.78; 68.67; H 7.40; 7.55; N 5.28; 5.25
 $C_{15}H_{17}O_3N$. Calculated %: C 68.94; H 7.33; N 5.36

Oxidation of the diacetyl derivative of 4-p-tolylaminobut-2-en-1-ol to N-acetyl-N-p-tolylglycine

A solution of 4.7 g (0.03 moles) of potassium permanganate in 300 ml of dry acetone was added during 165 min. with continual stirring to a solution of 2.61 g (0.01 moles) of the diacetyl derivative of 4-p-tolylaminobut-2-en-1-ol in 100 ml of dry acetone. The precipitate was collected on the following day, washed with acetone, and extracted with 50 ml of water. The aqueous extract was extracted with chloroform and was then made acid with dilute hydrochloric acid. The precipitate was collected, washed with cold water, and dried in a desiccator over sulfuric acid, to give 1.15 g (56% yield) of N-acetyl-N-p-tolylglycine, m.p. 173-176°, rising to 175.5-177° after recrystallization from hot water. Published m.p. data are 174-175° [3] and 175-176° [4].

Found %: C 63.79; 63.69; H 6.31; 6.34; N 6.79; 6.92
 $C_{11}H_{13}O_3N$. Calculated %: C 63.75; H 6.33; N 6.76

The mixed m.p. with a specimen of N-acetyl-N-p-tolylglycine, m.p. 175-177°, prepared by oxidizing N-allylacet-p-toluidide with potassium permanganate in acetone, was 175-177°.

Conversion of 2-p-tolyl-3,6-dihydro-orthoxazine into 1-p-tolyl-2,5-dihydropyrrole

25 g of zinc dust was added to a solution of 17.5 g (0.1 moles) of 2-p-tolyl-3,6-dihydro-orthoxazine in 50 ml of glacial acetic acid, in a round-bottomed 250 ml flask fitted with a reflux condenser. The flask was shaken, when its contents became very hot, leading to vigorous boiling lasting for some minutes. The mixture was then boiled for 5 hrs., 100 ml of water was added to the cooled mixture, which was made alkaline with 40% caustic soda, and was steam distilled. Nearly colorless crystals separated from the distillate, and were collected and dried over sulfuric acid; 10.9 g (69% yield) of 1-p-tolyl-2,5-dihydropyrrole, m.p. 87-90°, were thus obtained. The m.p. rose to 92-93° after two recrystallizations from methanol.

Found %: C 83.06; 83.14; H 8.24; 8.24; N 8.68; 8.56
 $C_{11}H_{13}N$. Calculated %: C 82.97; H 8.23; N 8.80

Conversion of 4-p-tolylaminobut-2-en-1-ol into 1-p-tolyl-2,5-dihydropyrrole

A mixture of 17.7 g (0.1 moles) of 4-p-tolylaminobut-2-en-1-ol, 10 g of anhydrous zinc chloride, and 50 ml of glacial acetic acid was boiled under reflux for 5 hrs., 100 ml of water and 100 g of sodium hydroxide were added to the cooled solution, and 1-p-tolyl-2,5-dihydropyrrole was distilled over with steam, and dried over sulfuric acid; yield 11.4 g (71%), m.p. 87-90°, raised to 92-93° by twice recrystallizing from methanol.

Oxidation of 1-p-tolyl-2,5-dihydropyrrole with potassium permanganate, to give 1-p-tolylpyrrole

A solution of 4.7 g (0.03 moles) of potassium permanganate in 300 ml of dry acetone was added, with

constant stirring, during 2½ hrs to a solution of 4.78 g (0.03 moles) of 1-p-tolyl-2,5-dihydropyrrole in 100 ml of dry acetone. The solution was filtered on the following day, and the acetone was distilled off from the filtrate. 50 ml of dilute (1:1) hydrochloric acid was added to the residue, which was then steam-distilled. The 1-p-tolylpyrrole collecting in the distillate was collected, washed with water, and dried over sulfuric acid; yield 2.20 g (47%), m.p. 81-83°, raised by recrystallization from methanol to 82-83°.

The product gave no depression of the m.p. of 1-p-tolylpyrrole, m.p. 82-83°, prepared from N-mucyl-p-toluidine. Published m.p. data are 82° [5] and 79-79.5° [6].

Oxidation of 1-p-tolyl-2,5-dihydropyrrole with ferric chloride, to give 1-p-tolylpyrrole

13.5 g (0.02 moles) of ferric chloride hexahydrate in 50 ml of water was added with stirring to a solution of 3.18 g (0.02 moles) of 1-p-tolyl-2,5-dihydropyrrole in 60 ml of 1:1 hydrochloric acid, and the mixture was steam distilled after an hour, to give 2.62 g (83% yield) of 1-p-tolylpyrrole, m.p. 82-83°, unchanged by recrystallization from ethanol. It did not depress the m.p. of a known specimen of 1-p-tolylpyrrole.

Reduction of 2-p-tolyl-3,6-dihydro-orthoxazine with sodium in ethanol, to give N-crotyl-p-toluidine

Experiment 1. 50 g (about 2.2 g-atoms) of sodium was added in large lumps during 10 min. to a boiling solution of 35.0 g (0.2 moles) of 2-p-tolyl-3,6-dihydro-orthoxazine in 650 ml of absolute ethanol in a round-bottomed 3 l. flask fitted with a reflux condenser, and the mixture was heated until all the sodium dissolved. It was then cooled and made acid with 1:1 hydrochloric acid, and steam distilled. It was then made alkaline with 40% caustic soda, and again steam distilled, collecting the light yellow oil which separated from the distillate, and extracting the aqueous layer of the distillate with 3 successive 100 ml portions of ether. The ether extract was added to the oil, and the solution was dried with anhydrous sodium sulfate. The ether was distilled off, and the residue was fractionally distilled in vacuum, giving 22.3 g of N-crotyl-p-toluidine, b.p. 96-97°/3 mm, d_4^{20} 0.9458; n_D^{20} 1.5505; found MR_D 54.34; calculated MR_D 52.53; EMR_D 1.81. Yield 69%. N-Crotyl-p-toluidine is a colorless, fairly mobile liquid, gradually becoming yellow; according to the literature its b.p. is 135°/33 mm [7].

Found %: C 81.85; 81.76; H 9.38; 9.27; N 8.55; 8.55

$C_{11}H_{15}N$. Calculated %: C 81.93; H 9.38; N 8.69

Experiment 2. 50 g (about 2.2 g-atoms) of sodium was added in large pieces during 10 min. to a boiling solution of 35.0 g (0.2 moles) of 2-p-tolyl-3,6-dihydro-orthoxazine in 700 ml of absolute n-butanol, in a 3 l. round-bottomed flask fitted with a reflux condenser with a broad inner tube. The mixture was then heated until all the sodium had dissolved; further manipulations were as in Experiment 1. 20 g of N-crotyl-p-toluidine was thus obtained, b.p. 96-97°/3 mm, d_4^{20} 0.9465; n_D^{20} 1.5505; found MR_D 54.30; calculated MR_D 52.53; EMR_D 1.77. Yield 62%.

Benzoylation of N-crotyl-p-toluidine

8.4 g (0.06 moles) of benzoyl chloride was added in 5 portions to 6.45 g (0.04 moles) of N-crotyl-p-toluidine in 40 g of 10% aqueous sodium hydroxide, during 20 min., shaking vigorously after each additional excess of benzoyl chloride was decomposed by heating. The benzoylation product was dissolved in ether, and the solution was washed successively with water, 5% aqueous sodium hydroxide, 5% hydrochloric acid, and again with water. The residue after distillation of ether was fractionally distilled in vacuum, giving 9.17 g of N-crotyl-benz-p-toluidide (IX), b.p. 168-170°/2 mm; d_4^{20} 1.0597; n_D^{20} 1.5781; found MR_D 83.09; calculated MR_D 81.26; EMR_D 1.83, yield 86%, a viscous, practically colorless liquid.

Found %: C 81.87; 81.90; H 7.29; 7.22; N 5.31; 5.20

$C_{13}H_{17}ON$. Calculated %: C 81.47; H 7.22; N 5.28

Acetylation of N-crotyl-p-toluidine

8.06 g (0.05 moles) of N-crotyl-p-toluidine and 15 ml of acetic anhydride were heated at 100° for 3 hrs under reflux. The acetic acid and anhydride were distilled off at 45 mm, and the residue was fractionally distilled at 3 mm, giving 9.20 g of N-crotyl-acet-p-toluidide (X), a colorless, viscous liquid, b.p. 120-120.5°/3 mm, d_4^{20} 1.0001; n_D^{20} 1.5292; found MR_D 62.71; calculated MR_D 61.77; EMR_D 0.94. Yield 91%.

Found %: C 77.08; 77.08; H 8.46; 8.47; N 7.16; 7.20

$C_{13}H_{17}ON$. Calculated %: C 76.81; H 8.43; N 6.89

Oxidation of N-crotyl-acet-p-toluidide to N-acetyl-p-tolylglycine

A solution of 4.7 g (0.03 moles) of potassium permanganate in 300 ml of dry acetone was added during 3 hrs. with constant stirring to 2.03 g (0.01 moles) of N-crotyl-acet-p-toluidide in 100 ml of dry acetone. The solution was filtered the next day, and the precipitate was washed with acetone and extracted with 50 ml of water. The aqueous extract was extracted with chloroform, made acid with dilute hydrochloric acid, and filtered. The precipitate was washed with cold water and dried in a desiccator over sulfuric acid; yield 0.56 g (27%) of N-acetyl-N-p-tolylglycine, m.p. 172-175°, rising to 175-177° after recrystallization from hot water, giving no depression with N-acetyl-N-p-tolylglycine, m.p. 175.5-177°, obtained by oxidation of the diacetyl derivative of 4-p-tolylaminobut-2-en-1-ol.

SUMMARY

1. The reaction between p-nitrosotoluene and buta-1,3-diene has been studied.
2. It has been shown that buta-1,3-diene adds on to p-nitrosotoluene according to the diene synthesis, to yield 2-p-tolyl-3,6-dihydro-orthoxazine.

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Institute of Organic Chemistry
Academy of Sciences USSR
M. V. Lomonosov Moscow State University

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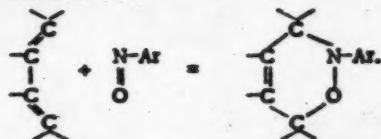
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REACTIONS OF DIENE HYDROCARBONS WITH NITROSO-COMPOUNDS

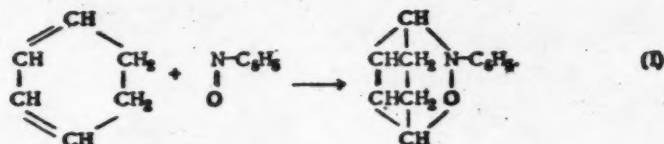
ADDITION OF CYCLOHEXA-1,3-DIENE TO NITROSOBENZENE

Yu. A. Arbuzov and T. A. Mastryukova

It has been shown in earlier communications [1,2] that buta-1,3-diene and other dienes (penta-1,3-diene, hexa-2,4-diene) condense with aromatic nitroso-compounds according to the diene synthesis, to give 3,6-dihydro-orthoxazine derivatives:



We shall in the present paper describe the results of a study of the reaction between cyclohexa-1,3-diene and nitrosobenzene, which should lead to the production of 2-phenyl-3,6-endoethyleno-3,6-dihydro-orthoxazine (I):



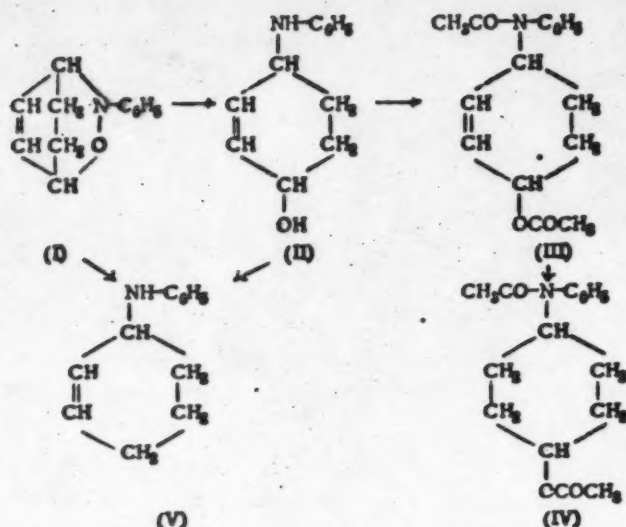
Cyclohexa-1,3-diene was prepared by the method of Ziegler [3], depending on bromination of cyclohexene with N-bromosuccinimide. We found that this was obtained in 67% yield only, applying Ziegler's method for bromination of succinimide, and his method was modified to give a 88% yield of N-bromosuccinimide. Bromination of cyclohexene with this gave 3-bromocyclohexene in 73% yield; elimination of hydrogen bromide by means of quinoline gave cyclohexa-1,3-diene in only 44% yield. Better results were obtained by the action of sodium acetate, which gave cyclohex-1-en-3-ol acetate in 89% yield, and this when heated with potassium bisulfate gave cyclohexa-1,3-diene in 66% yield.

Condensation of cyclohexadiene with nitrosobenzene proceeded smoothly in ether or ethanol at 0°, to give a colorless crystalline product, m.p. 65-66°, which was shown to be 2-phenyl-3,6-endoethyleno-3,6-dihydro-orthoxazine (I).

Reduction of the addition product with zinc dust in acetic acid gave a crystalline product, m.p. 64.5-65°, found to be 4-anilino-cyclohex-2-en-1-ol (II), acetylation of which with acetic anhydride afforded the diacetyl derivative (III), m.p. 56-57.5°. The presence of a double bond in compound (III) was shown by its catalytic hydrogenation, which gave the diacetyl derivative of 4-anilino-cyclohexan-1-ol (IV), m.p. 122-123°. (See top of next page).

It had previously been found [4] that reduction of 2-phenyl-3,6-dihydro-orthoxazine (produced by condensation of buta-1,3-diene with nitrosobenzene) with sodium in ethanol affords 1-anilinobut-2-ene, also obtained similarly from 4-anilinobut-2-en-1-ol (prepared by reduction of 2-phenyl-3,6-dihydro-orthoxazine with zinc dust and acetic acid).

Reduction with sodium in ethanol of 2-phenyl-3,6-endoethyleno-3,6-dihydro-orthoxazine (I) or of 4-anilino-cyclohex-2-en-1-ol (II) should afford 3-anilino-cyclohex-1-ene (V). This compound has not previously been described, and we synthesized it from 3-bromocyclohex-1-ene and aniline; its benzoyl derivative melted at 85-86°.



The expected amine (V) could not be isolated from the products of reduction of 2-phenyl-3,6-endoethyleno-3,6-dihydro-orthoxazine (I) with sodium in ethanol, which are a tarry mass. Reduction of 4-anilino-cyclohex-2-en-1-ol (II) with sodium in isoamyl alcohol gave a low yield of amine having a b.p. and refractive index close to those of 3-anilinocyclohex-1-ene (V), but the benzoyl derivative prepared therefrom melted at 72.5-74.5°. The reason for the difference in the melting points of the benzoyl derivatives may be that during reduction in isoamyl alcohol the double bond of the 3-anilinocyclohex-1-ene (V) formed may have undergone displacement. Noeldchen [5] observed this sort of isomerization during the reaction between sodium and 3-anilino-cyclopent-1-ene in isoamyl alcohol.

EXPERIMENTAL

Preparation of cyclohexa-1,3-diene

N-Bromosuccinimide. 17 ml of bromine was added during 80 min. to a solution of 32.0 g (0.323 moles) of succinimide and 12.8 g (0.32 moles) of sodium hydroxide in 70 ml of water, in a round-bottomed flask fitted with a stirrer and a dropping funnel, cooled in an ice-salt freezing mixture. The N-bromosuccinimide separating was collected, washed with 80 ml of ice water, and dried in a desiccator over calcium chloride, giving 50.8 g (89% yield) of N-bromosuccinimide.

3-Bromocyclohex-1-ene. A mixture of 150 ml of carbon tetrachloride, 82.1 g (1 mole) of cyclohexene, and 42.6 g (0.24 g-atoms of active bromine) was heated on a water bath for 90 min., in a round-bottomed flask fitted with a reflux condenser. The cooled solution was filtered, to remove succinimide, which was washed with 50 ml of carbon tetrachloride. The filtrate + washings were distilled, to remove carbon tetrachloride and unreacted cyclohexene, and the residue was fractionally distilled in vacuum to give 28.1 g (yield 73%) of 3-bromocyclohex-1-ene; b.p. 78-79°/39 mm.

Cyclohexa-1,3-diene. A mixture of 18.5 g (0.12 moles) of 3-bromocyclohex-1-ene and 46.5 g (0.36 moles) of freshly distilled quinoline in a 100 ml distilling flask fitted with a short fractionating column was heated in a metal bath at 140-150°, rising towards the end of the distillation to 170°; the receiver was immersed in freezing mixture. The distillate was washed with dilute hydrochloric acid and with water, and was dried over calcium chloride in presence of quinol, and then distilled from sodium, giving 4.08 g of twice-distilled cyclohexa-1,3-diene, b.p. 79.5-80°/736 mm; d_4^{20} 0.8394; n_D^{20} 1.4750; found MR_D 26.87; calculated MR_D 26.77. Yield 44%.

3-Acetoxycyclohex-1-ene. A mixture of 29.5 g (0.36 moles) of freshly fused sodium acetate, 120 ml of glacial acetic acid, and 40 g (0.25 moles) of 3-bromocyclohex-1-ene was left for 36 hrs, after which it was diluted with 350 ml of water, and made neutral with soda. The upper layer separating was washed with water, dried with fused caustic potash, and fractionally distilled in vacuum, to give 31.0 g (89% yield) of 3-acetoxycyclohex-1-ene, b.p. 58-59°/9 mm; d_4^{20} 1.0020; n_D^{20} 1.4588; found MR_D 38.24; calculated MR_D 38.13.

Cyclohexa-1,3-diene. A 50 ml distilling flask fitted with a short fractionating column and containing 30.2 g (0.215 moles) of 3-acetoxy-cyclohex-1-ene and 3 g of freshly fused potassium bisulfate was heated at 145-155°, cooling the receiver in a freezing mixture. The distillate was redistilled from 2 g of potassium bisulfate, and the distillate was washed successively with water, 5% caustic soda, and water, dried over calcium chloride in the presence of quinol, and again redistilled, giving 11.3 g (66% yield) of cyclohexa-1,3-diene, b.p. 80-80.5°/739 mm; d_4^{20} 0.8409; n_D^{20} 1.4751; found M_R 26.83; calculated M_R 26.77.

Preparation of nitrosobenzene

65 g of zinc dust was added in small portions during 20 min. to a mixture of 25 g of ammonium chloride in 800 ml of water and 50 g (42 ml) of nitrobenzene in a round-bottomed 1500 ml flask fitted with a mechanical stirrer; the temperature rose to 65° by the end of the reaction. The zinc oxide formed was filtered off and washed with 150 ml of hot water. The filtrate + washings were placed in a freezing mixture, when crystals of β -phenylhydroxylamine separated, and 130 ml of concentrated sulfuric acid was added when the temperature of the system had fallen to -2°, the mixture was shaken, replaced in the freezing mixture, and crushed ice was added to the solution of β -phenylhydroxylamine sulfate so obtained. A solution of 30 g of sodium dichromate in 100 ml of water at 0° was added rapidly to this solution when its temperature had fallen to -5°, the container was shaken for a few minutes, and the nitrosobenzene formed was collected on the filter pump, washed with water, and steam-distilled, cooling the receiver in ice. The nitrosobenzene collecting in the receiver was separated on the filter, washed with water, and dried in a desiccator over calcium chloride, giving 23.7 g (55% yield) of nitrosobenzene, m.p. 65-66°, not requiring any further purification.

Condensation of cyclohexa-1,3-diene with nitrosobenzene

Experiment 1. A flask containing 5.35 g (0.05 moles) of nitrosobenzene, 5.00 g (0.06 moles) of cyclohexa-1,3-diene, and 50 ml of ether was placed in an ice bath. Glistening crystals of the addition product began to appear within 2 hrs, and the reaction was completed within 24 hrs. The ether was then distilled off, and the product was recrystallized from ethanol, giving 8.45 g (90% yield) of a colorless microcrystalline product, m.p. 65-66°. 2-Phenyl-3,6-endoethyleno-3,6-dihydro-orthoxazine is readily soluble in hot methanol, ethanol, acetone, and cyclohexane, but is practically insoluble in water.

Found %: C 76.90; 76.95; H 7.00; 7.03; N 7.36; 7.47
 $C_{12}H_{13}ON$. Calculated %: C 76.97; H 7.00; N 7.48

Experiment 2. A mixture of 5.35 g (0.05 moles) of nitrosobenzene in 80 ml of ethanol and 5.00 g of cyclohexa-1,3-diene was kept at 0° for 24 hrs, the ethanol was distilled off on the water bath, and the residue was recrystallized from methanol, giving 8.05 g (86% yield) of 2-phenyl-3,6-endoethyleno-3,6-dihydro-orthoxazine, m.p. 65-66°.

4-Anilincyclohex-2-en-1-ol (II)

8 g of zinc dust was added in 4 portions during 25 min., shaking vigorously after each addition, to a solution of 3.7 g (0.02 moles) of 2-phenyl-3,6-endoethyleno-3,6-dihydro-orthoxazine in 40 ml of glacial acetic acid, in a 100 ml bottle. 20 ml of water was then added, the solution was filtered, and the precipitate was washed with 30 ml of hot benzene. The filtrate was made neutral with aqueous sodium hydroxide, and the hot solution was extracted with 3 portions of benzene, the benzene was distilled off, and the residue was fractionated in vacuum, giving 3.6 g (90% yield) of 4-anilincyclohex-2-en-1-ol, b.p. 168-168.5°/3.5 mm, 172.5-173.5°/5 mm, which crystallized after long standing. The m.p. was 64.5-65.5° after recrystallization from 1:1 ether-cyclohexane mixture.

Found %: C 76.22; 76.42; H 8.00; 7.96; N 7.32; 7.26
 $C_{12}H_{13}ON$. Calculated %: C 76.16; H 7.99; N 7.40

The picrate was prepared from ethereal solution, and was recrystallized from ethanol, m.p. 142.5-143.5°.

Found %: N 13.43; 13.59
 $C_{12}H_{13}O_2N_4$. Calculated %: N 13.39

Diacetyl derivative of 4-anilincyclohex-2-en-1-ol (III)

A solution of 8.5 g (0.045 moles) of 4-anilincyclohex-2-en-1-ol in 40 ml of acetic anhydride was heated

at 100° under reflux for 3 hrs, acetic acid and excess of acetic anhydride were distilled off at 50 mm, and the residue was distilled at 3.5 mm, giving 12.0 g (98% yield) of the diacetyl derivative of 4-anilinocyclohex-2-en-1-ol, b.p. 181-182°/3.5 mm, a colorless viscous liquid which crystallized after long standing, m.p. after recrystallization from cyclohexane 56-57.5°

Found %: C 70.41; 70.59; H 6.99; 6.95; N 5.00; 4.93
C₁₆H₁₉O₃N. Calculated %: C 70.30; H 7.01; N 5.12

Diacetyl derivative of 4-anilinocyclohexan-1-ol (IV)

8.2 g (0.03 mole) of the diacetyl derivative of 4-anilinocyclohex-2-en-1-ol in 90 ml of dry ether was hydrogenated in presence of 1 g of platinized charcoal (10% Pt) at room temperature and ordinary pressure, 672 ml of hydrogen (at N.T.P.) being absorbed during 50 min. The solution was filtered from the catalyst, and the ether was distilled off. The crystalline residue was recrystallized from ligroin, to give 7.2 g (87% yield) of the diacetyl derivative of 4-anilinocyclohexan-1-ol, m.p. 122-123°.

Found %: C 69.90; 69.92; H 7.69; 7.57; N 4.88; 4.88
C₁₆H₁₉O₃N. Calculated %: C 69.79; H 7.69; N 5.08

Reduction of 4-anilinocyclohex-2-en-1-ol (II) with sodium in isoamyl alcohol

10.5 g of sodium is added in a few portions to a boiling solution of 5.5 g (0.03 mole) of 4-anilinocyclohex-2-en-1-ol in 220 ml of anhydrous isoamyl alcohol, in a liter flask fitted with a reflux condenser, and boiling was continued until all the sodium had dissolved. The solution was cooled and made acid with hydrochloric acid, and isoamyl alcohol was removed by steam distillation, and the residual solution was made alkaline with potash, and extracted with benzene. The benzene was distilled off, and the residue was vacuum distilled, to give 0.68 g of a product of b.p. 146-147°/13 mm, n_D^{20} 1.5803 (benzoyl derivative, m.p. 72.5-74.5°, from ethanol).

3-Anilinocyclohex-1-ene (V)

A solution of 20.4 g (0.127 mole) of 3-bromocyclohex-1-ene in 45 ml of absolute ether was added in small portions to 36.8 g (0.39 mole) of freshly distilled aniline. A precipitate formed immediately, and the solution became hot enough to boil gently. Sufficient 10% caustic soda was added the next day to dissolve the precipitate, the ether layer was separated, the aqueous layer was extracted with ether, the combined ethereal solutions were dried with fused caustic potash, the ether was distilled off, and the residue was fractionally distilled in vacuum, giving 18.3 g (83% yield) of 3-anilinocyclohex-1-ene, b.p. 132.5-133°/7 mm; d_4^{20} 1.0222; n_D^{20} 1.5804; found M_R 56.42; calculated: M_R 54.95; EMR_D 1.47.

Found %: C 83.30; 83.32; H 8.83; 8.93; N 7.85; 7.78
C₁₂H₁₃N. Calculated %: C 83.18; H 8.73; N 8.09

Benzoyl derivative of 3-anilinocyclohex-1-ene

2.1 g (0.015 mole) of benzoyl chloride was added in 3 portions, with vigorous shaking after each addition, to 1.7 g (0.01 mole) of 3-anilinocyclohex-1-ene suspended in 7 ml of 10% caustic soda. The precipitate was washed with water, and was recrystallized from ethanol, giving 1.97 g (72% yield) of the benzoyl derivative of 3-anilinocyclohex-1-ene, m.p. 85-86°.

Found %: C 82.31; 82.42; H 6.84; 6.88; N 5.09; 5.00
C₁₉H₁₉ON. Calculated %: C 82.28; H 6.90; N 5.05

SUMMARY

1. The reaction between cyclohexa-1,3-diene and nitrosobenzene has been studied.
2. It was found that the reaction proceeds according to the diene synthesis, with formation of 2-phenyl-3,6-endoethyleno-3,6-dihydro-orthoxazine.

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Institute of Organic Chemistry
Academy of Sciences USSR, and
M. V. Lomonosov Moscow State University

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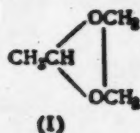
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* See Consultants Bureau Translation, p. 337. ** See Consultants Bureau Translation, p. 523.

SYNTHESES OF ACETALS OF ETHYLENE GLYCOL

M. F. Shostakovsky, N. A. Gershtein, and Z. S. Volkova

The acetals of ethylene glycol are undoubtedly of considerable theoretical and practical interest. Many derivatives of ethylene glycol, in particular its ethers are widely applied in various branches of industry and in laboratory practice [1-3]. The Russian scientists Markovnikov [4], Eltekov [5], and Favorsky [6] made important contributions to our knowledge of the properties of the α -glycols, including their general tendency towards isomerization into the appropriate aldehydes and ketones, including, in particular, the pinacolin rearrangement, and the mechanism of these transformations was elucidated [7]. These studies were also of practical significance, such valuable substances as Favorsky's dioxan, the importance of which can scarcely be overestimated, being obtained incidentally. Favorsky showed that a cyclic acetal (I) is formed at the same time as dioxan:



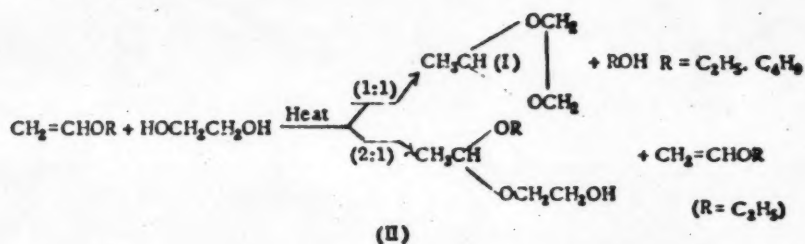
In spite of the symmetrical structure of the ethylene glycol molecule, it behaves in many reactions as a compound possessing two hydroxy groups of different reactivity, necessitating the provision of different conditions for preparation of its mono- and di-substituted derivatives, such as its mono- and di-ethers and -esters [8-13], or the mono- and di-alkylacetals.

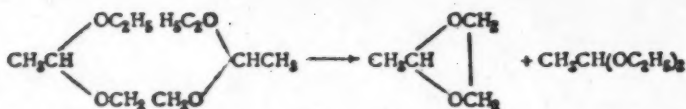
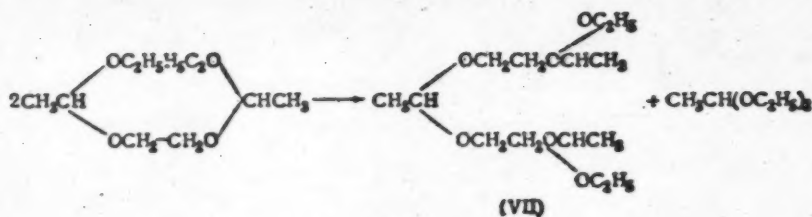
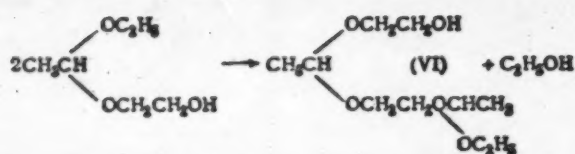
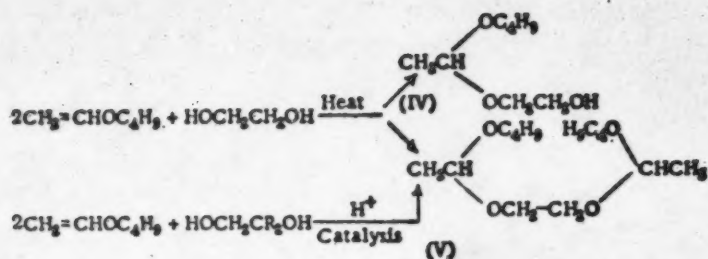
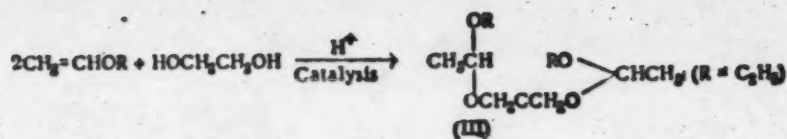
The latter group of substances is the subject of the present paper. The reason for the apparent non-equivalence of the hydroxy groups of ethylene glycol is that the reaction proceeds in stages. The symmetry of the molecule is abolished by formation of the mono-derivative, and the introduction of new radicals or groups also affects the reactivity of the remaining hydroxy group.

The alkylacetals of ethylene glycol were prepared by the method previously described by us, from monohydric alcohols and vinyl ethers [14-15]. The monoalkylacetals were prepared by the thermal method, and the dialkylacetals mostly by the catalytic method. The reaction leading to production of the cyclic acetal

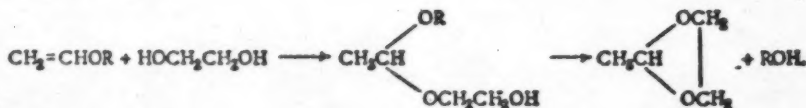
proceeds very easily. Monoalkylacetals are obtained from vinyl ether and ethylene glycol when they are taken in the molar ratio 2:1, whereas when they are taken in equimolecular proportions the substance (I) is obtained instead of the expected monoalkylacetal. The dialkylacetals of ethylene glycol were obtained when ethylene glycol containing catalyst was added to the vinyl ether; adding the catalyst to the ether, or to the glycol-ether mixture, led to production of methyldioxan (I).

The reactions involved in the synthesis of alkylacetals of ethylene glycol may be represented by the following equations:

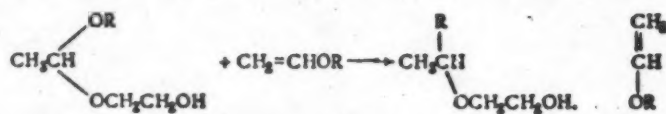




It is very probable that acetalization of one of the hydroxy groups of ethylene glycol causes enhancement of the activity of the hydrogen atom of the remaining one, thus leading to cyclization of the monoacetal with elimination of alcohol:



Presence of excess of vinyl ether evidently favors formation of a hydrogen bond, which hinders transformation of the monoacetal into a cyclic acetal:



According to Shostakovsky's oxonium theory [17,18,19] presence of H ions in catalytic reactions activates the molecules of vinyl ethers, with formation of oxonium complexes, thanks to which the reaction proceeds more energetically, and involves both of the hydroxy groups of ethylene glycol.

EXPERIMENTAL

Synthesis of β -hydroxyethylethylacetal (II)

A mixture of 144 g (2 mole) of vinyl ethyl ether, b.p. 35.6-36°/760 mm, (n_D^{20} : 1.3378; d_4^{20} 0.7531) and 62 g (1 mole) of ethylene glycol, b.p. 92.5°/8 mm; n_D^{20} 1.4320, was heated in a rotatory stainless steel autoclave, capacity 0.5 l., for 12-15 hrs. at 200-225°, pressures of 25-35 atm. being developed. The product was a homogeneous, mobile, straw-yellow liquid, weighing 194.6 g, losses due to vaporization of excess of vinyl ether amounting to 11.4 g.

The product was fractionally distilled in vacuum in a stream of nitrogen previously passed through alkaline pyrogallol solution, concentrated sulfuric acid, and alkali, successively. Two products were isolated, β -hydroxyethylethylacetal (II), b.p. 59.2-60°/2.5 mm (91.15 g, 68% yield), and the substance (VI), b.p. 129-130°/2 mm (7.75 g, 7% yield of ethylene glycol).

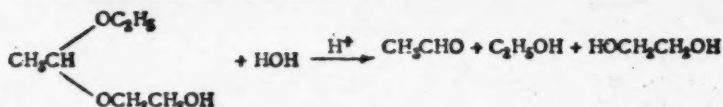
β -Hydroxyethylethylacetal has the following constants: b.p. 59.2-60°/2.5 mm, 55.75°/2 mm; n_D^{20} 1.4180; d_4^{20} 0.9753; M_R 34.64; calculated for $C_6H_{14}O_3$ M_R 34.719; found M 132.4; 132.6; calculated M 134.2.

Found %: C 53.80; 53.71; H 10.48; 10.54

$C_6H_{14}O_3$. Calculated %: C 53.73; H 10.45

β -Hydroxyethylethylacetal has not previously been described. It is a colorless, odorless, mobile, transparent liquid, soluble in ether, and benzene, readily soluble in ethanol and water, and reacting fairly energetically with sodium. Its structure was established by hydrolysis, with determination of the aldehyde, and by synthesis from it, as the alcoholic component, of acetal by the action of vinyl ethyl ether.

Hydrolysis of β -hydroxyethylethylacetal



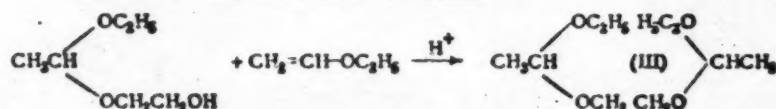
Hydrolysis with 2% sulfuric acid did not proceed to completion in the cold, the yields amounting to 88-94%. The method used by us was to heat the acetal in a sealed ampoule with 50 ml of 2% sulfuric acid for 2-4 hrs at 100°. The contents of the ampoule were then transferred to a volumetric flask, adding water to the mark, and taking 10 ml of the resulting solution for determination of acetaldehyde.

Acetaldehyde was determined by adding approximately 0.2 N sodium bisulfite, excess of which was titrated with 0.1 N iodine solution.* A sample of 0.5703 g of substance was hydrolyzed, and the volume of the product was made up to 200 ml. 4.25 ml of 0.1 N iodine was used to titrate 10 ml of the solution, corresponding with a value of 99.89% of the theoretical value. Results were calculated from the formula:

$$\% \text{ acetal} = \frac{(a-b) \cdot MK}{V \cdot 200}$$

where a is the number of ml of 0.1 N I_2 used in a blank titration, b is the number of ml of 0.1 N I_2 used in titration of excess of bisulfite, M is the mol. wt., K is the correction factor for the iodine solution (0.9662), and V is the weight of substance taken.

Acetalization of β -hydroxyethylethylacetal



* The method of determination is described in reference [16].

A drop of 33% hydrochloric acid was added as catalyst to a mixture of 34 g (0.25 mole) of β -hydroxy-ethylethylacetal and 18 g (0.25 mole) of vinyl ethyl ether. The reaction proceeded with liberation of heat, the temperature rising from 22° to 78°. The mixture was shaken from time to time, until the temperature ceased to rise, after which it was left overnight. The mixture was then fractionally distilled in a stream of nitrogen, giving 35.15 g (67.8% yield) of pure product (II), b.p. 85-85.5°/5 mm; 67.5-68° at 2 mm; n_D^{25} 1.4112; d_4^{25} 0.9274; MR_D 55.15; calculated for $C_{11}H_{22}O_4$ MR_D 54.952. Found M 189-190.8; calculated M 206.3.

Found %: C 57.80; 57.80; H 10.69; 10.85
 $C_{11}H_{22}O_4$. Calculated %: C 58.25; H 10.68

Compound (III) is further described below, in the paragraph dealing with its synthesis from ethylene glycol. The preparation of the diacetal has been described in a Patent specification, which gave only the b.p. 97°/13 mm [20].

β -Hydroxyethyl- β -ethoxyethylideneoxyethylacetal (VI) is a colorless, odorless, transparent liquid, soluble in ether, and very soluble in ethanol and water, very hygroscopic, b.p. 129-130°; n_D^{25} 1.4408; d_4^{25} 1.063; MR_D 55.13; calculated for $C_{11}H_{22}O_5$ MR_D 55.163. Found mol. wt., determined cryoscopically in benzene solution, 224.8; 221, calculated for $C_{11}H_{22}O_5$, 222.3.

Found %: C 51.70; 51.92; H 9.95; 10.00
 $C_{11}H_{22}O_5$. Calculated %: C 54.05; H 9.91

The difference between the actual and the theoretical analytical values is ascribable to the hygroscopicity of the product, and to possible formation of a hemihydrate, for which % C would be 51.85, and % H 9.96. This assumption is supported by the following facts: (a) repeated distillations always give a small amount of water, and (b) the product at first reacts very energetically with sodium, but the reaction soon slows down, usually taking 2-3 days for completion.

Analysis of the freshly distilled product gives a higher C content, although it is still less than the theoretical.

Found %: C 52.33; 52.40; H 9.84; 9.88
 $C_{11}H_{22}O_5$. Calculated %: C 54.05; H 9.91

Hydrolysis is incomplete in the cold, being to only 90-91%, as compared with 98.92%, calculated from the composition $C_{11}H_{22}O_5 \cdot \frac{1}{2} H_2O$, when the product is heated in a sealed bulb, as described above.

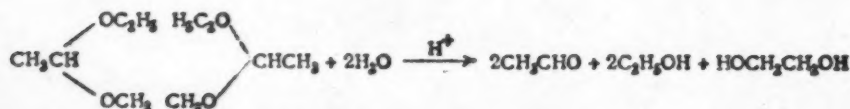
Synthesis of the diethylacetal of ethylene glycol (III)

The reaction, which was catalyzed by 33% of hydrochloric acid, was conducted in a flask fitted with a reflux condenser, a mechanical stirrer with a mercury seal, a thermometer, and a dropping funnel. Ethylene glycol containing 0.025-0.05 g of hydrochloric acid per 0.5 mole of compound (III) was added drop by drop to vinyl ethyl ether in the flask; an inverse-order of addition of the components converted the reaction towards production of the cyclic acetal (I). The experimental conditions are given in the Table. Two products were obtained in all cases; the expected dialkylacetal (III) and a higher b.p. product (VII).

The acetal (III) had the following physical constants: b.p. 92°/9 mm; 86° at 6 mm; n_D^{25} 1.4110; d_4^{25} 0.9274; MR_D 55.14; calculated for $C_{11}H_{22}O_4$ MR_D 54.952, cryoscopically determined molecular weight (in benzene) 190.9, 203.8, calculated M 206.3.

Found %: C 57.91; 58.32; H 10.75; 10.78
 $C_{11}H_{22}O_4$. Calculated %: C 58.25; H 10.68

Hydrolysis of the dialkyldiacetal of ethylene glycol (III)

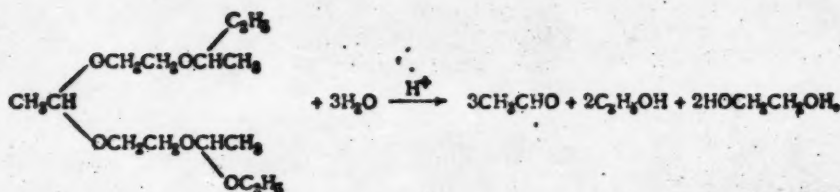


Hydrolysis was performed without heating, in stoppered Erlenmeyer flasks, in which the sample was shaken with 25 ml of 2% sulfuric acid and 25 ml of approximately 0.2 N NaHSO_3 until dissolution is complete, when it was left for 15 min., and excess of bisulfite was titrated with 0.1 N iodine. The content of diethylacetal of

ethylene glycol (III) thus found was 98.59% and 99.57% of the theoretical value, calculated for (III). The diethylacetal of ethylene glycol (VII) had b.p. 149.5-150°/2 mm; n_D^{20} 1.4235; d_4^{20} 0.9747; MR_D 76.81; calculated for $C_{14}H_{20}O_6$ 76.710. Found M 277.3; 280.0; calculated M 294.

Found %: C 57.34; 57.11; 57.00; H 10.41; 10.32; 10.28
 $C_{14}H_{20}O_6$ Calculated %: C 57.14; H 10.20

Hydrolysis of the diethylacetal of ethylene glycol, which proceeds according to the equation



shows that our product contains 97.80% or 97.65% of substance (VII).

The results agree with the formula proposed for the substance. In addition to the products enumerated, an additional fraction, boiling over the range of temperatures from 168° to over 200°, with partial decomposition, and of which the highest b.p. fractions partially solidified in the condenser, was obtained. The latter fraction, amounting to a yield of about 1.5%, was not further investigated.

Synthesis of β -hydroxyethylbutylacetal (IV)

Experiment 1. β -Hydroxyethylbutylacetal was synthesized similarly to β -hydroxyethylethylacetal (II). The cyclic acetal (I) was obtained instead of the expected acetal when vinyl n-butyl ether and ethylene glycol were taken in equimolecular proportions. 53 g of vinyl n-butyl ether, b.p. 93.2-93.8°/76 mm; n_D^{20} 1.4026; d_4^{20} 0.7790 and 31 g of ethylene glycol, b.p. 96°/7 mm; n_D^{20} 1.4320, gave after the first fractionation: Fraction 1, obtained by cooling the condenser spiral to -14-15°, at 2 mm: 29.57 g; n_D^{20} 1.3982;

Fraction 2, b.p. up to 35°/2 mm; 36.17 g; n_D^{20} 1.4018.

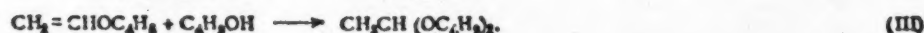
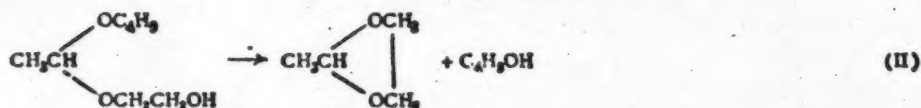
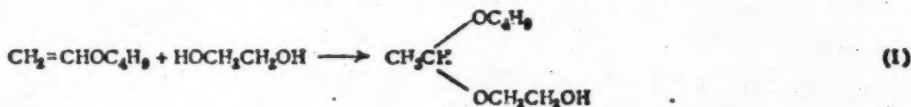
Residue in the distilling flask, separating into two layers, 6.20 g.

Fraction 1, after treatment with sodium, gave 28 g of the cyclic acetal of ethylene glycol, b.p. 81.5-82.5°, n_D^{20} 1.3975; d_4^{20} 0.9823; found MR_D 21.64; calculated for $C_6H_{10}O_2$ MR_D 21.758.

Fractional distillation of fraction 2 at atmospheric pressure gave 35.6 g of butanol, b.p. 116-118°; n_D^{20} 1.3995. The residue gave 2.7 g of dibutylacetal, b.p. 181-184°/758 mm; n_D^{20} 1.4080, and 1.7 g of butanol, b.p. 115-120°. The reaction thus gave:

- 1) $\begin{array}{c} \text{OCH}_3 \\ \diagup \quad \diagdown \\ \text{CH}_2\text{CH} \\ \diagdown \quad \diagup \\ \text{OCH}_3 \end{array} \dots 28.0 \text{ g (68.6\% of theory)};$
- 2) $\text{C}_4\text{H}_9\text{OH} \dots 37.3 \text{ g (95\% of theory)};$
- 3) $\text{CH}_3\text{CH}(\text{OC}_4\text{H}_9)_2 \dots 2.7 \text{ g (5.86\% of theory)}.$

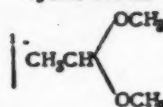
These data show that the reaction may be represented by the equations:



TABLE

Synthesis of the diacetal of ethylene glycol

Expt. No.	Ratio of reagents		Moles of HCl catalyst (30%)	% Yield of basic product	% Yield of by-product	Method of treatment of the reaction products and of isolation of the individual fractions	Remarks
	$\text{CH}_2=\text{CH}-\text{O}-\text{C}_2\text{H}_5$ moles	$\text{HOCH}_2-\text{CH}_2\text{OH}$ moles					
1	1	0.5	$42 \cdot 10^{-3}$	11.41	2.95	Vacuum distillation without neutralization of the catalyst	Addition of vinyl ethyl ether to ethylene glycol. Basic product is (I).
2	1	0.5	$42 \cdot 10^{-3}$	68.98	18.84	ditto	Addition of ethylene glycol to vinyl ethyl ether
3	2	1	$42 \cdot 10^{-3}$	61.22	7.3	"	ditto
4	2	1	$42 \cdot 10^{-3}$	66.6	20.1	Neutralization of catalyst with solid K_2CO_3 and vacuum distillation of filtrate	"
5	2	1	$42 \cdot 10^{-3}$	63.4	17.2	ditto	"
6	2	1	$42 \cdot 10^{-3}$	42.88	12.31	Neutralization with 2% K_2CO_3 , washing with water, drying over K_2CO_3 , and vacuum distillation	"
7	2	0.5	$42 \cdot 10^{-3}$	65.97	12.95	Treatment of the reaction products with sodium, followed by vacuum distillation	"
8	0.5	0.5	$42 \cdot 10^{-3}$	-	-	Vacuum distillation	Sole product is the cyclic acetal



NOTE. It appears from the Table that the best yields are obtained with a ratio of reagents of 2:1, adding ethylene glycol + catalyst to vinyl ethyl ether. The opposite order of addition, and also a ratio of 1:1, as in Expts. 1 and 8, lead to formation of cyclic acetal.

Experiment 2. Experimental conditions as above, but the ratio of vinyl n-butyl ether to ethylene glycol was 2:1 mol. 100 g of vinyl n-butyl ether and 31 g of ethylene glycol gave 127.6 g of liquid product (losses 3.4 g), the first fractionation of which gave:

Fraction 1, b.p. 26-30° at 8 mm, 31.17 g (condenser spiral cooled to -14°)

Fraction 2, b.p. 32-72° at 3 mm, 10.53 g.

Fraction 3, b.p. 73-85° at 3 mm, 5.73 g.

Fraction 4, b.p. 138-147° at 3 mm, 58.31 g.

Fraction 5, b.p. 163-234° at 3 mm, 13.00 g with decomposition.

Fraction 1, after treatment with sodium, gave 28.5 g of vinyl n-butyl ether, b.p. 93-93.6° at 758 mm n_D^{20} 1.4025. Similar treatment of Fractions 2 and 3 gave 9.8 g (about 6% of theoretical) of dibutylacetal, b.p. 183-186°; n_D^{20} 1.4088.

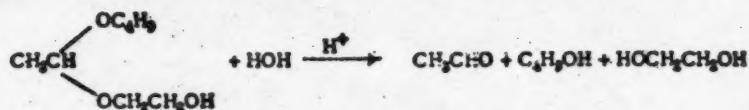
Triple fractionation of Fraction 4 gave two products, one of which was β -hydroxyethylbutylacetal (IV) (17.5 g, or 21.6% of theoretical yield), while the other was the dibutylidiacetal of ethylene glycol (V) (21.2 g, or 10% of theoretical yield). Prolonging the reaction time did not lead to production of higher yields of the products.

β -Hydroxyethylbutylacetal is a colorless, transparent liquid, b.p. 78-79° at 2 mm; 92-93° at 3 mm; n_D^{20} 1.4250; d_4^{20} 0.9435; MR_D 43.88; calculated for $C_8H_{16}O_3$, MR_D 43.955; found M 161.3; 161.4; calculated M 162.22.

Found %: C 59.40; 59.19; H 11.20; 10.98
 $C_8H_{16}O_3$. Calculated %: C 59.26; H 11.11

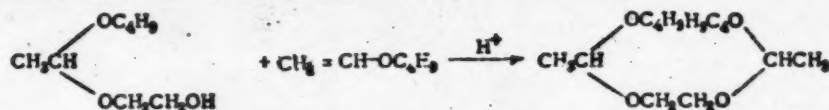
The structure of substance (IV) was established by its hydrolysis, and by the synthesis from it of substance (V), by reaction with vinyl n-butyl ether.

Hydrolysis of β -hydroxyethylbutylacetal proceeds in accordance with the equation



under the same conditions as for the preceding product, and indicate a content of β -hydroxyethylbutylacetal (IV) of 98.31% or 99.03%.

Acetalization of β -hydroxyethylbutylacetal



9.5 g of substance (IV) and 6.0 g of vinyl n-butyl ether in presence of catalyst gave 12.8 g of substance (V), a yield of 85.5%. It had b.p. 120.5-121° at 2 mm; n_D^{20} 1.4220; d_4^{20} 0.9072; MR_D 73.50; calculated for $C_{14}H_{28}O_4$, MR_D 73.424; found M 274.8; 274.2; calculated M 262.4.

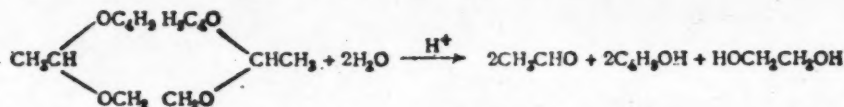
Found %: C 64.85; 64.38; H 11.64; 11.58
 $C_{14}H_{28}O_4$. Calculated %: C 64.13; H 11.45

The structure of compound (V) has thus been established in two ways, and is beyond doubt.

Compound (V), obtained in the synthesis of compound (IV), has b.p. 120-121° at 2 mm; 128-129° at 2.5 mm; 137-138° at 3 mm; n_D^{20} 1.4220; d_4^{20} 0.9095; MR_D 73.20; calculated for $C_{14}H_{28}O_4$, MR_D 73.424; found M 254.7; 256.8; calculated M 262.4.

Found %: C 63.81; 63.94; H 11.60; 11.61
 $C_{14}H_{28}O_4$. Calculated %: C 64.13; H 11.45

Hydrolysis of the dibutylacetal of ethylene glycol (V)



showed a content of compound (V) of 97.88% or 98.3%.

It was not possible to separate individual fractions of the higher b.p. fractions, as they undergo decomposition even at pressures of the order of hundredths of a mm.

Catalytic synthesis of the dibutylacetal of ethylene glycol (V)

Two experiments were performed, applying the same conditions as for synthesis of the diacetal (III). The reaction products of the first experiment, without preliminary neutralization of the catalyst, were fractionally distilled under reduced pressure in a stream of nitrogen. In the second experiment the catalyst was first neutralized with solid potassium carbonate.

Experiment 1. 93 g (1.5 mole) of ethylene glycol with 2 drops of 33% hydrochloric acid was added drop by drop to 300 g (3 mole) of vinyl n-butyl ether. The reaction products were fractionated under reduced pressure, in a stream of nitrogen. The first fractionation gave the following results:

Fraction 1, b.p. 20-21°/4 mm, 73.9 g; n_D^{20} 1.4008 (condensed in a spiral cooled at -14° to -15°).
 Fraction 2, b.p. 21-66°/4 mm (bulk at 64-66°), 47.4 g, n_D^{20} 1.4055.
 Fraction 3, b.p. 66°/4 mm, 154.6 g; n_D^{20} 1.4147.
 Fraction 4, b.p. 125-135° at 3 mm (bulk at 133-135°); n_D^{20} 1.4227.
 The residue of 20.5 g decomposes at its b.p.

Fraction 1, after treatment with sodium, gave 72.0 g of cyclic acetal of b.p. 81.5-82°; n_D^{20} 1.3987; d_4^{20} 0.9798; MR_D 21.67; calculated for $C_6H_{10}O_2$ MR_D 21.758.

Fractions 2 and 3 when similarly treated with sodium gave 176.3 g of dibutylacetal, b.p. 64°/2.5 mm; n_D^{20} 1.4090.

Fractions 4, after two redistillations, gave 65 g of the dibutyldiacetal of ethylene glycol (14% yield, calculated on ethylene glycol taken), b.p. 128°/2.5 mm; n_D^{20} 1.4222; d_4^{20} 0.9079; MR_D 73.33; calculated for $C_{14}H_{22}O_4$ MR_D 73.422.

Experiment 2. The experimental conditions were the same as before, taking 93 g of ethylene glycol (1.5 mole), and 300 g (3 mole) of vinyl n-butyl ether. After completion of the reaction the product was treated with anhydrous potassium carbonate, in order to neutralize the catalyst, filtered, and the filtrate was fractionally distilled as before. The results of the first fractionation were:

Fraction 1, b.p. 20-21°/40 mm (in the condenser spiral), 19.87 g; n_D^{20} 1.4070.
 Fraction 2, b.p. 40°/40 mm, 11.80 g; n_D^{20} 1.4090.
 Fraction 3, b.p. 101-105°/42-45 mm, 64.35 g; n_D^{20} 1.4125.
 Fraction 4, b.p. 125-172° at 42 mm, 229.0 g; n_D^{20} 1.4235.
 Residue 36.25 g; n_D^{20} 1.4145.

The first three fractions were shaken with 2% potassium carbonate solution, and then repeatedly with water, dried with anhydrous potassium carbonate, and redistilled, giving 25.6 g of dibutylacetal, b.p. 182-185°; n_D^{20} 1.4085.

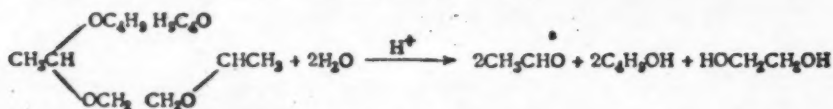
Repeated redistillation of Fraction 4 gave 35 g of a substance with the physical constants of compound (V). The bulk of Fraction 4 was dibutylacetal.

Product (V) from both experiments, after redistillation, boiled at 128-130°/2.5 mm; n_D^{20} 1.4220; d_4^{20} 0.9075; MR_D 73.36; calculated for $C_{14}H_{22}O_4$ MR_D 73.424; found M 251.8; 256.3; calculated M 262.3.

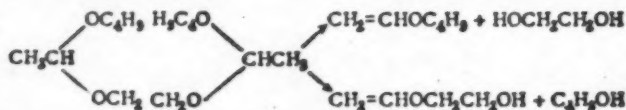
Found %: C 64.27; 64.11; H 11.62; 11.47

$C_{14}H_{22}O_4$. Calculated %: C 64.13; H 11.45

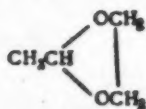
Hydrolysis of the dibutyldiacetal of ethylene glycol (V)



gave values of 98.6 or 99.82% of theoretical for the composition of compound (V). Thus we see that the reaction between vinyl butyl ether and ethylene glycol in presence of HCl catalyst leads to production of the dibutyldiacetal of ethylene glycol (V), although only in 15% yield. The results indicate that the diacetal (V) is very unstable, undergoing decomposition in two directions during distillation:



followed by cyclization, to give the acetal



and by formation of dibutylacetal by reaction between vinyl n-butyl ether and butanol. Evidently increase in the size of the radical R in ethylene glycol acetals with open chains renders them less stable.

SUMMARY

1. The conditions for synthesis of β -hydroxyethylalkylacetals have been worked out.
2. Conditions for synthesis of dialkylacetals have been elucidated.
3. Their tendency towards disproportionation with further transformations has been demonstrated.
4. Of the 6 compounds synthesized 5 have not previously been prepared or described.
5. A mechanism explaining the transformations is presented.

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Institute of Organic Chemistry
Academy of Sciences USSR

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SYNTHESIS AND POLYMERIZATION OF VINYLCAPROLACTAM

M. F. Shostakovsky, N. A. Medzykhovskaya, and M. G. Zelenskaya

The development of polymerization processes as a basis for production of high molecular substances has led to the intensive development of methods of synthesis of unsaturated compounds, and to a study of their chemical properties [1]. Vinyl ethers have assumed considerable importance during the past decade, and their synthesis has been based on the reaction of vinylation, introduced by Favorsky and Shostakovsky [2]. Attention was directed basically in these studies towards the reaction between acetylene and alcohols, and towards the investigation of the properties and transformations of the ethers obtained [2].

Much less attention has been devoted to the study of the products of reaction of acetylene with compounds containing nitrogen or sulfur. Most of the published references to nitrogen-containing vinyl derivatives and their polymers are in the patent literature, although this class of compounds is of considerable interest [3]. A study of the conditions of preparation of these compounds, and of their properties and characteristic reactions may provide us with a much more profound understanding of the mechanism of transformation of various vinyl derivatives.

Of the group of nitrogen-containing vinyl compounds N-vinylpyrrolidone [4] is of particular interest, in view of its polymer. It is synthesized usually in the following way:



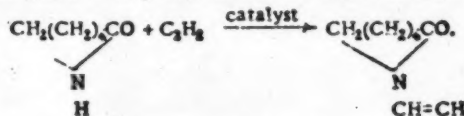
The polyvinylpyrrolidone molecule contains the carbamido-group, similarly to proteins:



Our studies included preliminary investigations of synthesis of pyrrolidone by the above reactions, as well as work on vinylcaprolactam and its polymer, since these are based on materials which are readily available, and which have been widely used in our industry.

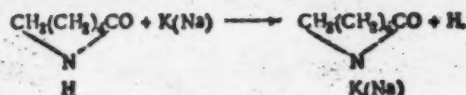
It may be supposed that polyvinylcaprolactam, the molecule of which also contains the carbamido-group, should possess a number of valuable properties. There are no references in the literature to polyvinylcaprolactam, and only brief references to vinylcaprolactam in the American patent literature, whereby vinylation of caprolactam is conducted in toluene solution by means of acetylene diluted with nitrogen, in presence of potassium salt of pyrrolidone as a catalyst. The vinylation of pyrrolidone and its derivatives (methylpyrrolidone) and homologs (piperidone and ϵ -caprolactam) was conducted in the presence of known catalysts of this process (alkalis, alkoxides) and of less widely known catalysts, such as salts of lactams, imides, and amides. Solvents which may be used in the process are toluene, decalin, and vinyl ethers [5].

In the preparation of vinylcaprolactam we took potassium hydroxide as the catalyst, as well as the potassium salt of ϵ -caprolactam, which we were the first to apply for this purpose. The solvents used were vinyl butyl ether or toluene. Vinylation proceeds only very slowly, even at 170–175°, using powdered potassium hydroxide as the catalyst and vinyl butyl ether as the solvent; the reaction mixture contained a large amount of unreacted ϵ -caprolactam, with tarry products, but only traces of vinyl compound. Much better results were obtained with potassium salt of ϵ -caprolactam as catalyst, when the yields of vinyl derivative were 71% of theoretical.



Vinylation was effected with undiluted acetylene, which was shown by Shostakovsky to give good results in the preparation of vinyl ethers. The vinylcaprolactam so obtained was a crystalline substance, which has not previously been reported. It is very hygroscopic, and when left in contact with the atmosphere it can absorb an equimolecular amount of water; the hydrate so obtained does not crystallize.

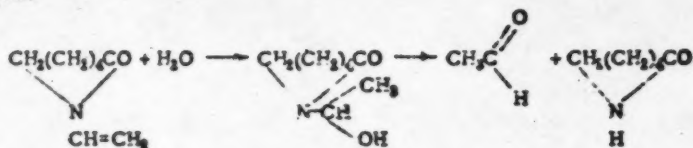
The product of reaction of potassium or sodium with such lactams as pyrrolidone is usually termed the potassium or sodium salt of the lactam, and we accordingly call our catalyst the potassium salt of ϵ -caprolactam:



We found that the amount of hydrogen evolved when potassium is added to ϵ -caprolactam is considerably less than would follow from the above equation, suggesting that much of it is used in some hydrogenation reaction. It might be supposed that the resulting products could be 6-aminohexanol ($\text{NH}_2\text{CH}_2-(\text{CH}_2)_4\text{CH}_2\text{OH}$), as well as hexamethylenimine $\text{CH}_2(\text{CH}_2)_4\text{CH}_2$ and other products. There are grounds for believing that these products are

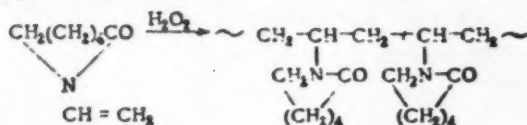
formed by the action of sodium on caprolactam in ethanol solution.

Hydrolysis of vinylcaprolactam with dilute sulfuric acid gives ϵ -caprolactam and acetaldehyde, through the semi-acetal:



ϵ -Caprolactam is obtained in small yields only from the reaction mixture, owing, in our opinion, to formation of water-soluble-aminocaproic acid and its salts; it is known that heating of ϵ -caprolactam with acids leads to formation of ϵ -aminocaproic acid $\text{H}_2\text{NHC}(=\text{CH}_2)_5\text{COOH}$ [6]. By subjecting ϵ -caprolactam to the action of acid, under the same conditions as for hydrolysis of vinylcaprolactam, we were able to recover only very small amounts of ϵ -caprolactam.

Vinylcaprolactam is not so readily hydrolyzable as are the vinyl ethers, suggesting that during vinylation ϵ -caprolactam reacts as a lactam, giving N-vinyl derivatives. It is known that with excess of reagent and at higher temperatures ϵ -caprolactam gives principally N-derivatives, and that O-derivatives when formed are transformed into N-derivatives when heated [8]. A fall in the yield of free aldehyde produced is observed when the temperature of hydrolysis is raised, due to the tendency of the aldehyde to condense with amino-acid, to give N-alkylidene derivatives. We did not in the present research make any more detailed study of the conditions of full hydrolysis of vinylcaprolactam. The process of polymerization of vinylcaprolactam is of considerable interest:



A preliminary test of the capacity for polymerization of vinylcaprolactam, taking as catalyst ferric chloride, which is widely applied to the polymerization of vinyl ethers [8] did not give the desired results; this is further evidence that our product is the N-vinyl, and not the O-vinyl derivative.

Formation of polymer was not observed with benzoyl peroxide at 55-60°; we found that activation of the vinylcaprolactam molecule by peroxides requires a temperature higher than 100°. The high temperature required for polymerization of vinylactams (vinylcaprolactam, vinylpyrrolidone) appears to be due to the lowering of the reactivity of the ethylene bond by presence in the molecule of the carbamido-group. We were able to effect polymerization of vinylcaprolactam in presence of hydrogen peroxide at 140-150°. The elucidation of the structure of the links of the resulting chain will be the subject of a special research. It should be noted that under our conditions of polymerization the reaction mixture finally obtained still contained monomer, which could be distilled off from the polymer, and redistillation of this monomer gave rise to formation of considerable amounts of polymer. This effect may be ascribed to presence in the monomer of traces of a volatile crystalline product formed from hydrogen peroxide and caprolactam in presence of air, and this product is, as will be shown below, an initiator of the polymerization process.

Polyvinylcaprolactam is a faintly yellow powder, readily soluble in cold water, benzene, and ethanol, but insoluble in ether and gasoline. When the aqueous solution of the polymer is heated the polymer separates out, returning into solution when the water cools; this shows that desolvation takes place.

A study of polymerization of aqueous emulsions, in the presence or absence of certain basic neutralizing substances (ammonia, amines), is of considerable importance. We were able to isolate a hitherto unknown crystalline intermediate product of polymerization of vinylcaprolactam, which gave peroxide reactions, and which was formed when vinylcaprolactam was heated with hydrogen peroxide with access of air. Determination of the molecular weight of this product suggests that it consists of two molecules of vinylcaprolactam and one of oxygen $C_{18}H_{28}N_2O_4$ (M 310). We were able to show that the product acts as an initial active center for the growth of the polymer chain, and is thus an initiator of the process of polymerization of unsaturated compounds, in particular of vinylcaprolactam.

It may be supposed that the process proceeds in two directions in presence of air. In one, the vinylcaprolactam molecule enters into reaction, after activation by peroxide (or rather by atomic oxygen arising from decomposition of peroxide), with other, inactive vinylcaprolactam molecules, to give polymer. In the other direction the active molecule reacts with atmospheric oxygen to give the above mentioned peroxide compound, which then breaks down and can initiate the polymerization process.

We have only the block polymerization of vinylcaprolactam over a narrow range of temperatures, and in presence of air. It would be of great interest to study this process in the absence of atmospheric oxygen, since this should lead to a considerable increase in its velocity, due to the exclusion of the possibility of formation of the intermediate peroxide product. Formation of polymer by thermopolymerization is insignificant at these temperatures (140-150°).

EXPERIMENTAL

Preparation of vinylcaprolactam

A solution of 198 g of ϵ -caprolactam in about 200 g of toluene is put into a stainless steel rotary 2000 ml autoclave containing catalyst, and fitted with a manometer, a thermometer, and a micro-valve for introduction of gas. The catalyst is prepared from 28 g of ϵ -caprolactam in 150 ml of toluene and 9.7 g of potassium at 60-80°. The total charge of the autoclave, in g., is

ϵ -caprolactam	226
Toluene	400
Potassium	9.7

The amount of caprolactam taken for preparation of the catalyst amounts to 12-12.5% of the total taken for the reaction. The autoclave is filled with acetylene, and heated; absorption of acetylene proceeds energetically at about 100°, and heating is then stopped (maximum temperature 125°). The autoclave is allowed to cool, when a further charge of acetylene is given, and the temperature is again raised to 100-125°. These operations are repeated until there is no further absorption of acetylene.

The reaction mixture, which is a viscous brown mass, is transferred to a flask, the autoclave is washed out with 30 g of toluene, and the washings are added to the mixture, which is then fractionally distilled. After the toluene has been distilled off in vacuum, 215 g of a product boiling at 129-134°/24-25 mm is obtained, leaving 65 g of tarry residue. Redistillation gives 190.2 g of vinylcaprolactam, b.p. 131-132°/22 mm. Extraction of the tarry product with ether gives a further 9.2 g of vinylcaprolactam, b.p. 129-130°/20.5 mm, giving a total yield of vinylcaprolactam of 199.4 g, or 71%, calculated on the amount of ϵ -caprolactam taken (226 g). Part of the vinylcaprolactam obtained was distilled, using a laboratory column, type LKS, height of working section 600 mm, filled with glass rings of diameter 1.5 mm (15-20 theoretical plates). This distillation confirmed the purity of our product, which had the following constants: b.p. 95°/4 mm; d_4^{20} 1.0084; n_D^{20} 1.5051; found MR_D 40.890.

$C_9H_{17}NO$. Calculated MR_D (for N-vinyl)	40.428
Calculated MR_D (for O-vinyl)	40.795

Vinylcaprolactam is a colorless crystalline substance, m.p. 34-35°, with, however, a tendency towards remaining in the liquid state even when pure; rapid crystallization may be induced by mechanical factors, and is associated with evolution of heat. The substance is readily soluble in ether, ethanol, benzene, toluene, and gasoline.

	Found %	C 68.76; 69.10; H 9.17; 9.30
$C_7H_{13}NO$.	Calculated %	C 69.06; H 9.42
	Found %	N 10.00; 9.82
$C_7H_{13}NO$.	Calculated %	N 10.07
	Found M	138.50; 139.63
$C_7H_{13}NO$.	Calculated M	139.11

Hydrolysis of vinylcaprolactam

1. Two sealed bulbs each containing 20 ml of 4.5% sulfuric acid and 0.1954 or 0.2054 g of vinylcaprolactam were heated for 55 hrs. at 55-60°, well cooled before opening, and the contents were transferred quantitatively to 25 ml of a cooled solution of sodium bisulfate. Acetaldehyde formed was determined iodometrically after 30 min., by Ripper's method.

% Hydrolysis of vinylcaprolactam: (a) 81.1 (b) 78.7

2. Bulbs containing (a) 0.1031 (b) 0.1028 g of the substance, with 20 ml of 4.5% sulfuric acid in each, were heated in a thermostat for about 10 hrs at 80°, followed by 35 hrs at 110°; further treatment was as in Experiment 1.

% Hydrolysis of vinylcaprolactam: (a) 15.3 (b) 14.7.

3. (a) 10.01 g of vinylcaprolactam and 450 ml of 4.5% sulfuric acid were heated at 60° for 23-25 hrs in a flask fitted with a stirrer, a thermometer, and a condenser, connected with two cylinders containing sodium bisulfite solution; the final volume of the solution was 446 ml. 25 ml of bisulfite solution was added to 10 ml of the reaction mixture, and % hydrolysis was measured; it amounted to 63.2.

Alkali was added to the remaining solution until it had only a weakly acid reaction, and water was evaporated off under reduced pressure. Benzene extraction of the residue gave 0.2 g of a substance melting at 64-65°, shown to be caprolactam (no depression of m.p. of a known sample).

(b) 5 g of caprolactam and 50 ml of 4.5% sulfuric acid were heated under reflux in a round-bottomed flask for 20 hrs at 60°. Alkali was then added to a weakly acid reaction, water was eliminated under reduced pressure, and the residue was dried to constant weight (9.9 g). 1.5 g of caprolactam was extracted from the residue with benzene.

Polymerization of vinylcaprolactam

1. 7.1 g of vinylcaprolactam and 0.07 g of benzoyl peroxide were heated in a bulb for 40 hrs at 55-60°. Distillation of the mixture gave 7 g of the initial vinylcaprolactam, with a small amount of tarry matter.

2. 15.7 g of vinylcaprolactam and 0.25 g of 25% hydrogen peroxide were heated in a bulb for 10 hrs at 80°, and then for about 40 hrs at 110°. The reaction mixture, a brown liquid, was dissolved in gasoline, and the precipitated resin was repeatedly treated with gasoline, finally to give a small amount of a yellow powder, which was soluble in benzene, ethanol, and cold water, from which it is precipitated by heating. The yield of polymer was 1.5 g, being 1% of the amount of vinylcaprolactam taken. The polymer was reprecipitated from benzene solution.

Cryoscopic determination of molecular weight in benzene solution gave values of 871 and 1024.

The solution remaining after precipitation of the polymer was fractionally distilled in vacuum, after distilling off the solvent. The products were (a) vinylcaprolactam, b.p. 138-141°/31-33 mm, 9.7 g, (b) impure vinylcaprolactam, 1 g, and (c) tarry residue.

3. 31 g of pure vinylcaprolactam (b.p. 103-104°/5.5-6 mm) in a round-bottomed flask fitted with a stirrer, a thermometer, and a reflux condenser, was heated to 140°, and 32% hydrogen peroxide was added drop by drop during 19 hrs, a total of 0.77 g of hydrogen peroxide being added, or 2.4% of the amount of vinylcaprolactam. The reaction mixture was a brown, viscous liquid, from which 12 g of polymer was precipitated as a yellow powder by addition of ether. The filtrate gave a further 2.5 g of polymer, in the form of a semi-liquid resin, and 14 g of monomer, and reprecipitation of the resin gave 1.3 g of solid polymer, the total yield of which was thus 13.3 g, or 42.9% of the vinylcaprolactam taken. Redistillation of the 14 g of monomer recovered from the reaction mixture was associated with further polymerization, yielding 6 g of solid polymer, the total yield of which was thus raised to 19.3 g, or 62.2%.

4. 27 g of vinylcaprolactam was heated for 18-15 hrs at 140-150° with 0.5 g of catalyst in the apparatus described above. The catalyst was prepared by heating vinylcaprolactam with hydrogen peroxide, and is a crystalline substance. The reaction mixture was a dark brown liquid, from which 14 g of polymer was obtained by adding 200 ml of ether, this being a yield of 51.4%. The molecular weight of polymer precipitated from benzene by addition of ligroin was determined cryoscopically in benzene solution, values of 2855 and 2655 being obtained.

Polyvinylcaprolactam is a faintly yellow powder, readily soluble in cold water, benzene, and ethanol, and insoluble in ligroin and ether. It separates out from its aqueous solutions when they are warmed.

Product of reaction of vinylcaprolactam with hydrogen peroxide

32% Hydrogen peroxide (0.28 g) is added gradually to 34 g of vinylcaprolactam in a flask fitted with a reflux condenser, a stirrer, and a thermometer, at 100°; the temperature is raised during the first 90 min. to 150°, and then during the next hour to 170°. The crystalline product is cooled and extracted with ether, to separate it from the small amount of polymer formed, the ether is distilled off, as is unreacted vinylcaprolactam (16 g); owing to which the crystalline product dissolved in ether. When distilling off the ether we observed formation of a white deposit on the walls of the receiver, indicating that the crystalline product is somewhat volatile. The residue after distilling off monomer (12.1 g) is a viscous oil, treatment of which with ether gives 8 g of white crystalline substance, soluble in benzene and ethanol, sparingly soluble in water, ligroin, light petroleum, and ether. After recrystallization from hot water or light petroleum it melts at 144-145°.

Determination of molecular weight (cryoscopic method)

Found M: a) 309; b) 314; mean 311

Calculated for $C_{10}H_{17}NO_2$: M 310

The substance reacts as a peroxide, and acts as an initiator of the process of polymerization of vinylcaprolactam.

SUMMARY

1. A method for obtaining vinylcaprolactam in about 70% yield was found.
2. A new catalyst was used for vinylation of ϵ -caprolactam, viz., "the potassium salt of ϵ -caprolactam" (the product of reaction of potassium with ϵ -caprolactam).
3. Vinylcaprolactam is readily obtained in crystalline form; this is highly hygroscopic, and it absorbs an equimolecular amount of water when exposed to the air.
4. Hydrolysis of vinylcaprolactam gives acetaldehyde, ϵ -caprolactam, and salts of ϵ -aminocaproic acid.
5. Polymerization of vinylcaprolactam proceeds satisfactorily in presence of hydrogen peroxide at 140-150°.
6. A crystalline intermediate product of polymerization of vinylcaprolactam was isolated. It is formed by the action of oxygen on vinylcaprolactam, and it exhibits peroxide properties, and can serve as an initiator of the polymerization process.
7. The process of thermopolymerization of vinylcaprolactam proceeds only to a negligible extent.

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Institute of Organic Chemistry
Academy of Sciences USSR

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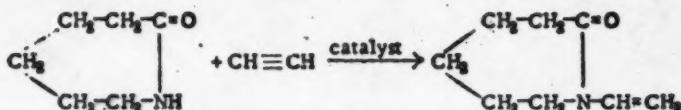
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SYNTHESIS AND TRANSFORMATIONS OF VINYLCAPROLACTAM

PART 1. POLYMERIZATION IN PRESENCE OF HYDROGEN PEROXIDE

M. F. Shostakovskiy, F. P. Sidelkovskaya, and M. G. Zelenskaya

N-Vinylcaprolactam is a compound of considerable interest; it may be prepared from caprolactam and acetylene in presence of alkaline catalyst [1]:



In the given case, as in that of vinylation of hydroxy-compounds [2], undiluted acetylene gives good yields. Favorsky and Shostakovskiy [2] successfully applied undiluted acetylene to synthesis of vinyl ethers of the type $\text{CH}_2=\text{CH}-\text{OR}$, as long ago as 1943; in spite of this, foreign workers still use acetylene diluted with inert gases for the purpose [3], although Favorsky and Shostakovskiy's method is generally and widely applied in the Soviet Union.

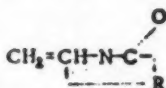
A method for production of vinylcaprolactam has recently been worked out in our laboratory [1], by heating caprolactam with acetylene, in toluene solution, with potassium salt of caprolactam as catalyst. The preparation of this catalyst presents, however, certain difficulties, associated with the use of metallic potassium, which so readily reacts with oxygen, with inflammation, on exposure to the air. Additional researches were undertaken in order to find a more readily prepared catalyst than the caprolactam salt, such as, in particular, potassium hydroxide. Although it was evident from preliminary experiments [1] that this catalyst did not give the desired results, it was nevertheless thought desirable to subject this catalyst to a more detailed examination. Potassium hydroxide was added either immediately before vinylation, or it was previously heated with caprolactam in an autoclave; in the latter case heating was at atmospheric pressure or at 150 atmospheres. Synthesis of vinylcaprolactam did not take place under any of these conditions.

Since potassium salt of caprolactam could not be replaced by potassium hydroxide, we next studied the effect of substituting metallic sodium for potassium, as being more convenient to handle. The sodium salt was found to be as effective a catalyst as is the potassium salt of caprolactam, the yields of vinylcaprolactam being 70-80% in both cases (see Experimental Section, below).

The reaction of vinylation was conducted using different solvents, viz., toluene, vinyl butyl ether, ligroin, and butanol. The reaction proceeds similarly in the first three solvents, the only differences being in the isolation and purification of the product. In the last case, it was thought that conjugated vinylation of caprolactam and of the solvent might take place, analogous to oxidation of difficultly oxidizable substances in presence of readily oxidized ones [4].

In spite, however, of variation of the reaction conditions (temperature, catalysts), vinylcaprolactam was not obtained, and vinyl butyl ether was only obtained in one case (temperature 140° , KOH catalyst) in small yield. It is evident that the simultaneous presence of caprolactam and butanol somehow leads to inhibition of the reaction of vinylation of both substances. We now recommend vinylation of caprolactam in ligroin solution, with its sodium salt as catalyst.

Vinylcaprolactam may be regarded as having the structure:



where R is a bivalent radical. In this respect it may be considered as an analog of vinyl esters of type (I), but not of ethers of type (II):



As could be expected from a consideration of the structure of vinylcaprolactam it has a tendency towards polymerization. It is relatively stable at ordinary temperatures, but it partly polymerizes when heated (100-150°), and gives high yields of polymer in presence of hydrogen peroxide [1]. The present research is devoted to the study of polymerization of vinylcaprolactam at different temperatures, in presence of the given catalyst; the results are shown in Table 1.

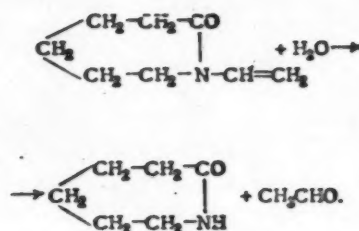
It appears from Table 1 that the velocity of polymerization falls parallel with temperature, and the amount of catalyst required rises. The optimum temperature is 140-150°, at which 33 μ of vinylcaprolactam undergoes polymerization during 7-9 hrs, with yields of about 70%. At 100-125° polymerization of about the same amount of vinylcaprolactam proceeds only to about 25-50% after 22-23 hrs. It also follows from the data of Table 1 that a relatively small change in temperature causes a fairly considerable change in the velocity of polymerization, with only slight change in the properties of the polymer. The specific viscosity of the polymers obtained over the range 100-150° is $\eta_{sp.} = 0.11-0.17$ (1 g/100 ml of benzene), and the mean molecular weight, determined cryoscopically in benzene, is 1000-1500.

It is of interest that at 100-125° acetaldehyde and caprolactam were formed together with the polymer. It is quite probable that the small amount of water introduced with the hydrogen peroxide was sufficient for effecting partial hydrolysis of vinylcaprolactam:

TABLE 1

Polymerization of vinylcaprolactam in presence of H_2O_2 (29% solution)

Expt. No.	Temp. °C	Duration in hours	Amount of 29% H_2O_2 solution, in g	Amount of polymer formed, as % of vinylcaprolactam taken	Amount of unreacted monomer, %	Mol. wt. (cryoscopically, in benzene)	$\eta_{sp.}$ (1 g in 100 ml benzene)
3	140-143	7	0.45	70	21	1602; 1715	0.1740
4	143-147	9	0.64	68.4	25.8	1209; 1070	0.1673
5	143-149	9	1.20	72.4	18.7	1235; 1394	0.1417
7	115-125	22	1.90	24.5	18.6*	Sparingly soluble in C_6H_6	0.1109
8	100-105	23.5	2.00	50	12.2*	—	0.1133



* Caprolactam and acetaldehyde were formed as well as polymer in these experiments.

EXPERIMENTAL

A. Vinylation of caprolactam in benzene solution

Catalyst: sodium salt of caprolactam.

a) Preparation of catalyst. 40 g of caprolactam and 1.86 g of sodium finely dispersed by Bruhl's method [7] in 50 ml of ligroin (b.p. 130-150°) are heated with constant stirring to complete dissolution of the sodium, which takes about an hour.

b) Vinylation is effected as usual in a rotating stainless steel autoclave. 45 g of caprolactam and 150 ml of ligroin (b.p. 100-120°) are added to the product obtained above, and the mixture is placed in a 2500 ml autoclave; the total charge was: caprolactam 77 g, Na salt of caprolactam 10 g, and ligroin 200 ml. The autoclave is filled with acetylene at a pressure of 15-18 atm., and the temperature is raised to 115-125°. The autoclave is then allowed to cool, a fresh charge of acetylene is added, and the autoclave is again heated. This operation is

repeated until somewhat more than the theoretical amount of acetylene has been absorbed. The mixture is then filtered, and the precipitate (16.3 g) is washed with five portions of ligroin. The solvent is distilled off from the filtrate + washings, at ordinary pressure, and the residue is fractionated under reduced pressure, to give 75.2 g (79.8% yield) of vinylcaprolactam, b.p. 119-121°/13 mm, n_D^{20} 1.5139, redistillation of which affords 73.8 g of product, b.p. 104-105.5°/7-7.5 mm; n_D^{20} 1.5138.

B. Polymerization of vinylcaprolactam

1. At 140-150°. 0.16 g portions of catalyst (20% aqueous H_2O_2) are added at $1\frac{1}{2}$ -2 hrs intervals, to a total of 1.20 g, to 32.6 g of vinylcaprolactam in a flask fitted with a mechanical stirrer, a thermometer, and a reflux condenser, immersed in an oil bath at 143-144°. Addition of each of the initial portions of catalysts was followed by a temperature rise of 15-20°, but the final portions gave hardly any thermal effect. The total duration of the process is 9 hrs, at an average temperature of 140-150°. The final reaction mixture is a light brown viscous liquid, which changes to a vitreous solid on cooling. Repeated extraction of this with dry ether gives 23.8 g of amorphous polymer of vinylcaprolactam, representing a yield of 72.4%, calculated on vinylcaprolactam taken for the reaction, or of 90% calculated on the amount actually reacted. Fractionation of the ether extracts gives 6.1 g of unreacted vinylcaprolactam, b.p. 104-107°/7 mm, and 2.3 g of vitreous polymer*.

TABLE 2

Data for fractionation of ethereal extracts of the polymerization product

Extract No.	Volume, ml	Amount of monomer, g	Amount of polymer, g
1	50	2.27	1.06
2	50	1.66	0.66
3	50	1.65	0.57
4	50	0.51	—
Total	200	6.09	2.29

The results of fractionation of the individual extracts are given in Table 2, from which it appears that the content of monomer is greatest in the first extract, and is very small in the fourth one; the polymer content falls in the same order. It is evident that the presence of monomer in the ether raises the solubility in it of the polymer.

The powdery polymer is dried in a vacuum desiccator to constant weight; its specific viscosity and molecular weight are: η_{sp} = 0.1417 (1 g/100 ml of benzene); M = 1293; 1394 (cryoscopically, in benzene).

2. At 115-125°. The reaction is conducted in the same apparatus as before, with the difference that the reflux condenser is connected to a series of three Tishchenko wash bottles, in order to absorb any acetaldehyde formed. 28% Hydrogen peroxide is added to 32.2 g of vinylcaprolactam at 115-125°, in small portions, as before. Only a slight temperature rise

is observed (2-3°) when the catalyst is added, in this case. The reaction product remains liquid for a very long time, and only after 22 hrs, and addition of 1.88 g of peroxide does it assume the consistency of a viscous resin. The product smells strongly of acetaldehyde, and it gives a positive reaction with fuchsin-bisulfite reagent. The reaction product is extracted with 5 portions of ether, giving 5.9 g of powdery polymer. The solvent is distilled off from the ethereal extracts, collecting the fraction boiling at 34-36°, and repeatedly extracting it with water. Titration of an aliquot part of the aqueous extract with sodium bisulfite gave 0.4 g of acetaldehyde, corresponding to 1.4 g, or to 4.3% of the vinylcaprolactam initially taken.** The tarry residue left after distilling off the ether was fractionated in vacuum, giving:

- 1) vinylcaprolactam (b.p. 98-99°/5 mm; n_D^{20} 1.5130) — 6 g (18.6%);
- 2) caprolactam (m.p. 60-62°, after recrystallization from ethanol 67-69°) — 3.75 g (14.3%) ***;
- 3) resinous polymer — 3.5 g, from which 2 g of powdery polymer was obtained by reprecipitation. The total yield of powdery polymer is thus 7.9 g, i.e. 24.5%.

Description of the polymer. The polymer is partly soluble in benzene. 2.91 g of polymer is treated with 20 ml of dry benzene, the residue is filtered off, and 80 ml of dry ether is added to the filtrate. The powdery precipitate is collected, washed with ether, and dried, giving 1.83 g of polymer (η_{sp} = 0.1109) (1 g of polymer in 100 ml of

*Further studies showed that the vitreous product is a mixture of the pure powdery polymer with monomer. It is not possible, in working with small amounts of vitreous polymer, to effect a satisfactory separation into its two components, since during reprecipitations a considerable part of the polymer remains in solution, under these conditions.

** Since it is not possible to recover all of the acetaldehyde forming during the reaction, percentage hydrolysis is calculated from the amount of caprolactam found.

*** The yield of reaction products is expressed as percentages of the amount of vinylcaprolactam taken for the reaction.

benzene); $M = 2818; 2364$ (cryoscopic method, in benzene).

3. At $100-110^\circ$. The apparatus and methods were as in Experiment 2. 28% peroxide is added to 24.5 g of vinylcaprolactam at $100-105^\circ$, and the temperature is maintained at $100-110^\circ$ for 23½ hours, during which time 2 g of catalyst is added, in all. Heating is then stopped, and a stream of nitrogen is passed through the system. Both the viscous polymerization product and the water in the wash bottles have a strong smell of acetaldehyde, and give a positive reaction with fuchsin reagent. Titration with sodium bisulfite of an aliquot part of the basic product gives an acetaldehyde content of 0.2 g, and of the water in the wash bottles a further 0.52 g, making 0.72 g in all. This corresponds with hydrolysis of 2.3 g of vinylcaprolactam.

Further confirmation of the presence of acetaldehyde in the wash bottle water was afforded by preparing its 2,4-dinitrophenylhydrazones, m.p. $162.5-163.6^\circ$, after recrystallization from ethanol.

The resinous basic reaction product is treated as in Experiment 2, giving:

- (1) powdery polymer - 12.1 g (50%);
- (2) unreacted monomer - 3 g (12.2%);
- (3) caprolactam - 8.4 g, corresponding to 8.6 g of vinylcaprolactam (27%).

The polymer is soluble in benzene, and its viscosity $\eta_{sp} = 0.1133$ (1 g of polymer in 100 ml of benzene).

SUMMARY

1. The preparation of vinylcaprolactam from acetylene and caprolactam is described; the sodium salt of caprolactam serves as a quite satisfactory catalyst.

2. Polymerization of vinylcaprolactam in presence of hydrogen peroxide has been studied over the range $100-150^\circ$. The velocity of polymerization rises, and the amount of catalyst required falls, as the reaction temperature is raised.

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Institute of Organic Chemistry
Academy of Sciences USSR

LITERATURE CITED

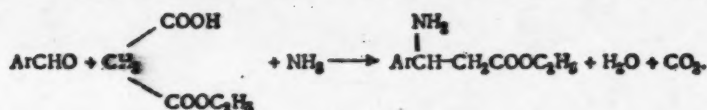
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NEW SYNTHESIS OF ALKYL ESTERS OF β -AMINO-ACIDS

V. M. Rodionov and N. N. Bezinger

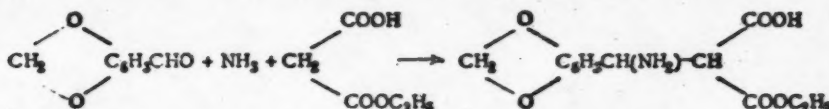
The new synthesis of β -amino-acid esters depending on reaction of aromatic aldehydes with malonic mono-ester in the presence of ammonia was undertaken because of the belief expressed in the older literature that the usual method cannot be applied to the preparation of β -amino-acids, as their tendency towards deamination would lead to the obtaining of very low yields. It was found later that this view is not always justified, since the deamination reaction was found to depend on the nature of the alkyl (or aryl) residue of the β -amino-acid, and on its structure. In many cases alkyl esters can be obtained in very good yield by heating alcoholic solutions of β -amino-acids with small amounts of concentrated sulfuric acid.

The method worked out for the synthesis of esters of β -amino-acids does not differ basically from that proposed by Rodionov and Malevinskaya [1] for the synthesis of β -amino-acids, or from the method for preparation of esters of β -aminoisosuccinic acid [2], i.e., the reaction proceeds according to the following general equation:

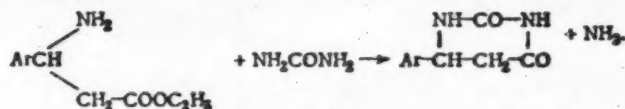


The alkyl esters of β -aryl- β -amino-acids are obtained in yields of 35-45%, and esters of arylacrylic acids are formed in yields of 40-45%. The ethyl esters of β -phenyl- β -alanine, β -piperonyl- β -alanine, and β -(3-nitrophenyl)- β -alanine were obtained by this method.

It is of particular interest that when piperonal is condensed with monoethyl malonate under mild conditions simultaneous decarboxylation does not take place, the product being monoethyl β -piperonyl- β -amino-isosuccinate. This confirms the correctness of the reaction mechanism:



Experiments were performed on the synthesis of ureido-derivatives of the esters obtained, in order to assist in their identification. The esters do not react with urea, however, to give the expected esters of β -ureidoacids, dihydrouracils being obtained instead. The reaction proceeds very readily, the dihydrouracils being obtained in good yield from the esters and a boiling aqueous solution of urea:



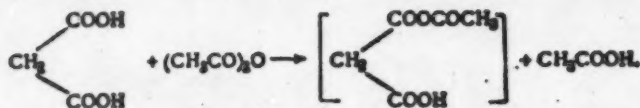
We know that free ureido-acids are converted into dihydrouracils with some difficulty, requiring boiling with hydrochloric acid.

The preparation of certain alkyl esters of β -amino-acids by the classical method is also described in this paper.

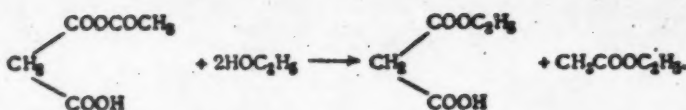
EXPERIMENTAL

Preparation of monoethyl malonate. There are two methods for preparation of monomethyl malonate. One, which was suggested by Van t'Hoff [3], and was worked out by Freund [4], consists of cautious hydrolysis of the diethyl ester with alcoholic caustic potash; the ethyl potassium salt crystallizes out in well-formed platelets after long standing of the solution. The crystals are treated with hydrochloric acid, and the solution is extracted with ether. The ether extract is dried with anhydrous sodium sulfate, the ether is distilled off, and the residue is dried at room temperature in a vacuum desiccator over anhydrous Na_2SO_4 , giving monoethyl malonate in 80% yield.

The second method was worked out by Vulfson [5]. Well dried malonic acid is dissolved in acetic anhydride (1:2 mol), and 24 hrs later excess of absolute ethanol is added, and the mixture is boiled for 1 hr. and then vacuum distilled, giving a 40% yield of monoethyl malonate. Vulfson supposes that the reaction proceeds according to the scheme:



The anhydride of malonic and acetic acids is unstable, and it reacts with ethanol giving ethyl acetate and monoethyl malonate:



We at first used Vulfson's method, but owing to its low yields we later on transferred to Van t'Hoff and Freund's method.

Preparation of monoethyl malonate by hydrolysis of diethyl malonate. A solution of 26.1 g of KOH in 300 ml of absolute ethanol is added drop by drop, with constant stirring, to a solution of 75 g of freshly distilled diethyl malonate in 300 ml of absolute ethanol, in a liter flask fitted with a stirrer with a mercury seal, and stirring is continued for 2 hrs after all the reagent has been added. A small amount of potassium malonate separates from the solution during the reaction, and is separated by bringing the solution to the boil, and filtering the hot solution. Large crystals of ethyl potassium malonate are deposited from the cooled filtrate, and they are collected on the filter, washed with dry ether, and dried in a vacuum desiccator; yield 68 g, or 85%.

68 g of ethyl potassium malonate is dissolved in 35 ml of water, and concentrated hydrochloric acid is added at 0°, with constant stirring, until the solution becomes acid to Congo red, when it is repeatedly extracted with ether. The ethereal extract is dried with anhydrous Na_2SO_4 , the ether is distilled off, and the residue is fractionally distilled in vacuum, collecting the fraction of b.p. 100-101°/4 mm. The yield of monoethyl malonate is 50.7 g, or 96% calculated on the basis of potassium salt, or 81.9% on that of diethyl malonate taken.

Synthesis of ethyl β -amino- β -phenylpropionate. 10 ml of a 15% solution of NH_3 in absolute ethanol is added to 12 g of benzaldehyde. The white precipitate of hydrobenzamide which separates when the first few ml of ammonia are added goes back into solution when the rest of the reagent is added. 11 g of monoethyl malonate is then added, this being associated with evolution of considerable heat, and the mixture is then heated at 100° until all the ethanol has distilled off, and until evolution of CO_2 has ceased (10 hrs). The resulting brown oil is treated with an equal volume of water, and the aqueous layer is extracted repeatedly with small portions of ether. The ethereal extracts are added to the oil residue, and the mixture is dried with anhydrous Na_2SO_4 . Long colorless needles separate from the residue during evaporation of the ether, which is continued until the volume of the solution is 1/3 of the initial value, when the precipitate is collected, washed with ether, and dried; 0.09 g of product, m.p. 144-145°, is obtained.

Found %: C 73.52; H 6.01; N 9.50

$\text{C}_9\text{H}_9\text{ON}$. Calculated %: C 73.44; H 6.16; N 9.52

The analytical results, and the properties of the product, correspond with cinnamamide, which, according to the literature, has m.p. 146-147°.

The mother liquor from the cinnamamide is dissolved in twice its volume of ether, and the solution is saturated with dry HCl, cooling in a freezing mixture. A yellow oil which at first separates solidifies later on. The hydrochloride of ethyl β -amino- β -phenylpropionate is collected, and washed with absolute ethanol, to remove HCl. The yield is 9.8 g, m.p. 137-147°. The product is soluble in hot ethanol, and insoluble in cold ethanol, ether, and water.

Attempts at purifying the hydrochloride were unsuccessful, the m.p. remaining indefinite after three recrystallizations (139-146°). We were not able to find any reference to the m.p. of this hydrochloride in the literature.

Posner found that β -phenyl- β -alanine formed, in addition to the ordinary monohydrochloride, an acid hydrochloride with 3 molecules of HCl, which was stable at the ordinary temperature, but evolved HCl when heated, and it may be that we obtained a mixture of the normal and the acid hydrochlorides; hence the indefinite m.p. of our product.

9 g of hydrochloride is made up into a paste with a little water, and 3% aqueous NaHCO_3 is added in small portions, with energetic stirring, giving a heavy, colorless oil. The supernatant aqueous layer is extracted with two portions of ether, and the extract is added to the oil, the solution then being dried with anhydrous Na_2SO_4 . The ether is evaporated off in vacuum, and the residue is fractionally distilled, collecting the fraction boiling at $116-119^\circ/7$ mm, which is redistilled, when 7.2 g (45% yield calculated on monoethyl malonate taken) of ester is obtained. Ethyl β -phenyl- β -alanine, b.p. $116-117^\circ/7$ mm, is a syrupy colorless liquid with a fairly pleasant odor.

Found %: N 7.08; 7.15

$\text{C}_{11}\text{H}_{15}\text{O}_2\text{N}$. Calculated %: N 7.25

Synthesis of ethyl β -amino- β -piperonylpropionate. 15 ml of a 15% solution of ammonia in absolute ethanol and 9.3 g of monoethyl malonate are added to 10.4 g of piperonal dissolved in a small volume of ethanol. Considerable heat is evolved, with vigorous production of CO_2 . The mixture is heated on the water bath until all the alcohol has distilled off, and until evolution of CO_2 ceases (15 hrs). The final product is a dense brown liquid, which is treated with twice its volume of hot water, and the aqueous layer is extracted with ether. The extract is added to the oily product, and the solution so obtained is dried with anhydrous Na_2SO_4 .

The dried solution gradually deposits a colorless crystalline product, which is collected, washed with cooled ether, and dried; yield 0.55 g, m.p. $69-70^\circ$, readily soluble in ether and acetone, sparingly soluble in ethanol, insoluble in water or aqueous sodium carbonate. The alcoholic solution decolorizes bromine water or KMnO_4 solution. The product does not contain nitrogen.

Found %: C 65.61; H 5.30

$\text{C}_{11}\text{H}_{12}\text{O}_4$. Calculated %: C 65.44; H 5.49

The product is ethyl β -piperonylacrylate, whose m.p. is reported in the literature as $67-68^\circ$ [5].

Saturation with dry HCl of the mother liquor from this product, with cooling in a freezing mixture, gives a yellowish precipitate of the hydrochloride of the ethyl ester of β -piperonyl- β -alanine, which is collected, washed free of HCl with absolute ethanol, and dried; yield 9.3 g, m.p. $182-183^\circ$.

8 g of hydrochloride is treated with 3% NaHCO_3 solution, at 0° , giving 7.5 g of ethyl ester of β -piperonyl- β -alanine, a yield of 45% calculated from monoethyl malonate taken, or of 69.8% calculated from hydrochloride taken. The syrupy product crystallizes after a few days, and the ester is recrystallized from ethanol, m.p. $70-71.5^\circ$. The ethyl ester of β -piperonyl- β -alanine is soluble in hot ethanol and ether, but not in water, alkalis, or acids.

Found %: N 5.81; 5.80

$\text{C}_{11}\text{H}_{15}\text{O}_4\text{N}$. Calculated %: N 5.90

A precipitate of some unknown substance was observed to form during the reaction, and then to disappear as the reaction proceeded towards completion. The reaction was repeated with certain modifications, in order to discover the nature of this product. Heating of the reaction mixture was not continued until no more CO_2 was evolved, but was stopped when the amount of precipitate appeared to be at a maximum. The precipitate was found to be an intermediate product of condensation of aldehyde with monoethyl malonate, viz., monoethyl β -amino- β -piperonylsuccinate.

A mixture of 17.5 g of piperonal, 19 g of monoethyl malonate, and 25 ml of 15% NH_3 in absolute ethanol was heated on a boiling water bath until all the ethanol had evaporated (5 hrs), although CO_2 was still being evolved. The reaction mixture then consisted of a dense brown liquid, with a considerable amount of white crystalline precipitate. It was treated with ether, which dissolved only the oily part, leaving the crystalline product, which is collected, washed with ether, and dried in a vacuum desiccator; yield 4.39 g, m.p. $115-116^\circ$ (decomp.). The product decomposes when heated, with evolution of CO_2 and NH_3 .

Found %: N 5.14; 5.16

$\text{C}_{13}\text{H}_{15}\text{O}_8\text{N}$. Calculated %: N 4.98

As in the preceding experiment, the ethereal extract was concentrated to a third of its volume, in order to obtain ethyl piperonylacrylate, which was not, however, formed. An equal volume of dry ether was then added, and the solution was saturated with dry HCl, giving 2.1 g of the hydrochloride of the ethyl ester of β -piperonyl- β -alanine.

Synthesis of ethyl β -amino- β -3-nitrophenylpropionate. A mixture of 13.1 g of *m*-nitrobenzaldehyde, 10.8 g of monoethyl malonate, and 15 ml of 15% alcoholic ammonia is heated on a boiling water bath until evolution of CO_2 ceases (10 hrs). A yellow precipitate forms at the beginning of the process, but disappears after two hours of heating. The brown oil obtained at the end of the reaction is treated with twice its volume of hot water, and the aqueous extract is extracted with a few small portions of ether; the ethereal extract is then added to the residual oil, the solution is dried with anhydrous Na_2SO_4 , and saturated with dry HCl. The yellow oil which separates soon crystallizes; it is collected, washed with dry ether, and dried, giving 10.1 g of the hydrochloride of the ethyl ester of β -(3-nitrophenyl)- β -alanine, m.p. 171-172°, insoluble in ether or cold ethanol, readily soluble in hot ethanol; yield 51.6%, calculated on monoethyl malonate taken.

10 g of the hydrochloride is treated with 3% NaHCO_3 solution at room temperature, when a yellow oil is obtained. This is separated, the aqueous layer is extracted a few times with ether, and the extracts are added to the oil. The resulting solution is dried with anhydrous Na_2SO_4 , the ether is evaporated off in vacuum, and the residual oil is cooled in ice water, when it crystallizes, giving 8.1 g of ethyl ester of β -(3-nitrophenyl)- β -alanine, m.p. 77-78°, yield 93% calculated on hydrochloride taken, or 44.6% calculated on monoethyl malonate taken.

Found %: C 55.61; 55.39; H 6.00; 5.73; N 11.56; 11.60
 $\text{C}_{11}\text{H}_{14}\text{O}_4\text{N}_2$. Calculated %: C 55.45; H 5.92; N 11.76

Preparation of 4-phenyldihydrouacil. 3 g of urea in 15 ml of water is added to a solution of 1 g of ethyl ester of β -phenyl- β -alanine in 5 ml of ethanol, and the mixture is boiled under reflux until evolution of ammonia ceases (15 hrs). Thin silky needles separate from the cooled solution; they are collected, washed with water, and dried, giving 0.32 g of 4-phenyldihydrouacil, m.p. 216-218°, soluble in cold water, cold ethanol, or ether, readily soluble in hot ethanol. The mixed m.p. with a known specimen of 4-phenyldihydrouacil, prepared by a different method, was 218-220°.

Preparation of 4-piperonyldihydrouacil. A mixture of 1 g of ethyl ester of β -piperonyl- β -alanine in 5 ml of ethanol and 3 g of urea in 15 ml of water is boiled under reflux until evolution of NH_3 ceases (24 hrs). The cooled solution deposits a precipitate of small glistening platelets, which is collected, washed with water, and dried, giving 0.47 g of 4-piperonyldihydrouacil, m.p. 236-237°.

The published m.p. of this product is 247°, but repeated recrystallizations of our product failed to raise its m.p.

Found %: C 56.56; H 4.21; N 11.78
 $\text{C}_{11}\text{H}_{14}\text{O}_4\text{N}_2$. Calculated %: C 56.40; H 4.30; N 11.96

Preparation of the ethyl ester of N-benzoyl- β -phenyl- β -alanine, by the classical method. 15.4 g of benzoyl chloride is added drop by drop, with constant stirring, to a solution of 16.4 g of β -phenyl- β -alanine in 170 ml of 10% caustic potash at -5° ; the temperature should at no time exceed 5° . The mixture is stirred for an hour after addition of the last drop of benzoyl chloride, and is then made acid with 1:1 hydrochloric acid. The product is collected on the filter, repeatedly washed with hot water, to remove benzoic acid, and recrystallized from boiling ethanol; yield 21.2 g (80% of theory).

20 g of N-benzoyl- β -phenyl- β -alanine is heated for 6-7 hrs under reflux on a boiling water bath with 100 ml of absolute ethanol and 4 ml of concentrated sulfuric acid, and about 50 ml of ethanol are then distilled off. The ethyl ester separates in the form of glistening needles from the cooled solution, and it is collected, washed, and dried. An equal volume of water is added to the filtrate, which is then made neutral with soda. The ethyl ester of N-benzoyl- β -phenyl- β -alanine which separates is collected, washed with water, and dried, and the combined precipitates are recrystallized from 50% ethanol; yield 18.9 g ($\sim 86\%$ of theory), m.p. 112-113°.

Found %: N 4.80; 4.82
 $\text{C}_{12}\text{H}_{15}\text{O}_3\text{N}$. Calculated %: N 4.72

The ethyl esters of N-benzoyl- β -(3-nitrophenyl)- β -alanine (yield $\sim 92\%$) and of N-benzoyl- β -piperonyl- β -alanine (yield 82%) were obtained in the same way.

SUMMARY

1. A new method is described for the preparation of ethyl esters of β -aryl- β -aminoacids, depending on condensation of monoethyl malonate with aromatic aldehydes in the presence of alcoholic ammonia.
2. The method serves for preparation of the ethyl esters of β -phenyl- β -alanine, β -(3-nitrophenyl)- β -alanine, and β -amino- β -piperonylpropionic acid, and of monoethyl β -amino- β -piperonylisuccinate.
3. The esters were converted into 4-aryldihydrouracils by boiling with urea solution.
4. Ethyl esters were prepared by the standard method from N-benzoyl derivatives of β -aminoacids.

Received March 25, 1952

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ACETYLENE DERIVATIVES

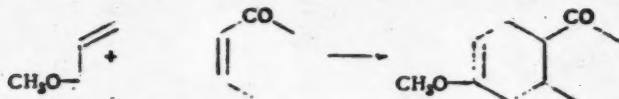
COMMUNICATION 127. SYNTHESIS OF POLYCYCLIC COMPOUNDS RELATED TO THE STEROIDS. XV. STRUCTURE OF THE PRODUCTS OF CONDENSATION OF 2-METHOXYBUTA-1,3-DIENE WITH 1-METHYLCYCLOHEX-1-EN-6-ONE AND METHYL METHACRYLATE

I. N. Nazarov and S. I. Zavyalov

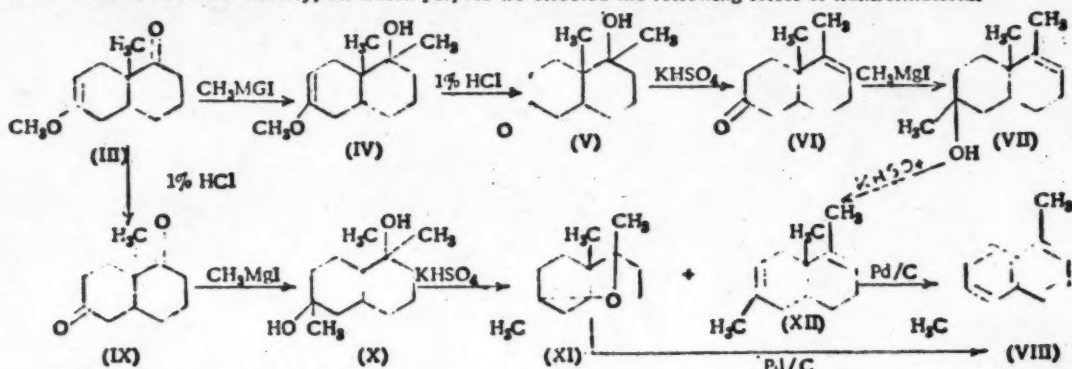
A general method has recently been worked out in our laboratory for the synthesis of polycyclic steroid ketones, with a hydrogenated cyclopentanophenanthrene structure, such as chrysene, cyclopentanofluorene, benzofluorene, and their heterocyclic thia analogs [1]. This synthetic method depended on condensation of bicyclic dienes with α, β -unsaturated cyclic ketones. The basic intermediate product in this synthesis is 6-methoxy-9-methyl- Δ^8 -octal-1-one (III), obtained by the condensation of 2-methoxybuta-1,3-diene (I) with 1-methylcyclohex-1-en-6-one (II):



The structure of the methoxyoctalone derivative (III) was derived from a study of condensations of 2-methoxybuta-1,3-diene with aliphatic α, β -unsaturated aldehydes, ketones, and acids, which in all cases yield *p*-substituted cyclic products [2]:



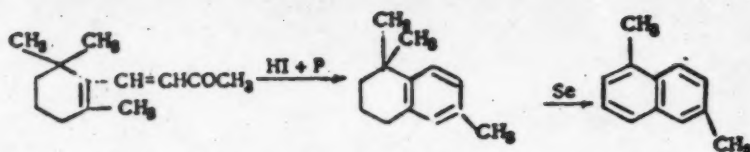
In view, however, of the exceptional importance of the methoxyoctalone (III), it was thought desirable to establish its structure directly, for which purpose we effected the following series of transformations:



Magnesium methyl iodide and the methoxyoctalone (III) gave a product which after treatment with dilute hydrochloric acid afforded 1,9-dimethyldecal-1-ol-6-one (V), readily dehydrated by potassium bisulfate to yield 1,9-dimethyl- Δ^1 -octal-6-one (VI), and this, by the action of magnesium methyl iodide, affords 1,6,9-trimethyl- Δ^1 -octal-6-ol (VII), which when dehydrated and dehydrogenated at a palladium-charcoal catalyst at 330-340° gives 1,6-dimethylnaphthalene (VIII). This was also prepared through the earlier described 1,6-diketo-9-methyldecalin

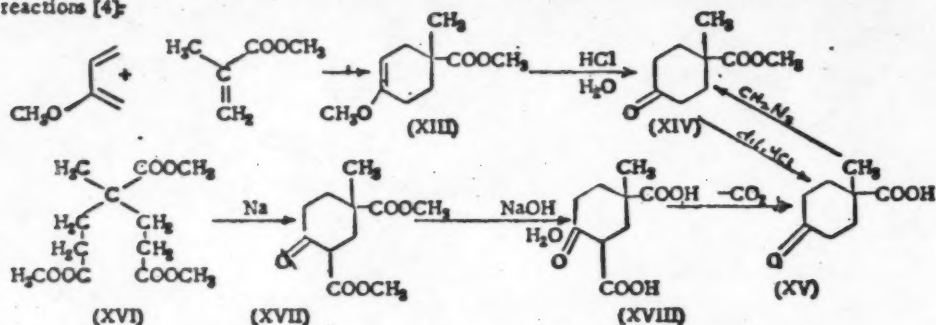
(IX), produced by the hydrolysis of the methoxyoctalone (III) with dilute hydrochloric acid. 1,6-Diketo-9-methyldecalin (IX) by a Grignard reaction with magnesium methyl iodide gives high yields of 1,6-dihydroxy-1,6,9-trimethyldecalin (X), dehydration of which with potassium bisulfate affords a mixture of the hydrocarbon (XII) and the oxide (XI), giving 1,6-dimethylnaphthalene (VIII) when dehydrogenated at a palladized charcoal catalyst.

In order to identify 1,6-dimethylnaphthalene it was synthesized from β -ionone by the following reactions [3]:



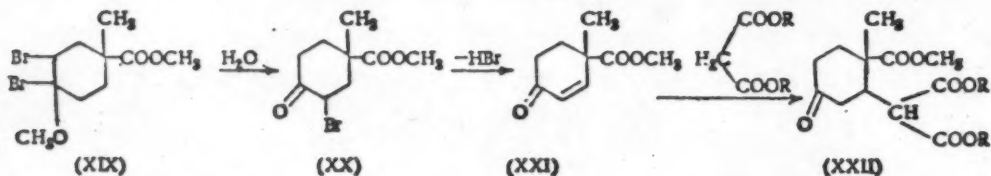
The product so obtained was in every way identical with that given by the methoxyoctalone (III); a mixture of their picrates showed no depression of m.p.

As we expected, methyl methacrylate condenses with 2-methoxybuta-1,3-diene, giving the para-isomer (XIII), the structure of which was established by converting it into the keto-acid (XV) and its methyl ester (XIV), and comparing these products with those obtained from 1,3,5-tricarbomethoxy-3-methyl-*n*-pentane by known reactions [4]:



The keto-acid (XV) and its ester (XIV) had identical properties; and the mixed m.p. of their semicarbazones and 2,4-dinitrophenylhydrazones showed no depression.

The methoxy-ester (XIII) may be of interest as a starting point for the synthesis of ketones of the hydrindane and decalin series with angular methyl groups. Bromination of the methoxy-ester (XIII) gives the dibromide (XIX), hydrolysis of which yields the bromo-keto-ester (XX), and hydrogen bromide is eliminated from this with production of the unsaturated keto-ester (XXI), addition to which of malonic ester affords the triester (XXII):



EXPERIMENTAL

6-Methoxy-9-methyl- Δ^8 -octal-1-one (III), b.p. 88-89°/0.1 mm; n_D^{20} 1.5089, was prepared by condensation of 2-methoxybuta-1,3-diene (I) with 1-methylcyclohex-1-en-6-one (II), as described before [1]. 1,6-Diketo-9-methyldecalin (IX), m.p. 63-65°, was prepared by hydrolysis of the methoxyoctalone (III) [1].

Action of magnesium methyl iodide on 6-methoxy-9-methyl- Δ^8 -octal-1-one (III)

A solution of 10 g of 6-methoxy-9-methyl- Δ^8 -octal-1-one (III) in 50 ml of absolute ether is added drop by drop, with constant stirring, and cooling in ice, to a Grignard reagent prepared from 1.8 g of magnesium and 13 g of methyl iodide in 50 ml of absolute ether, and the mixture is stirred at room temperature for a further 3 hrs, after which 50 ml of 5% hydrochloric acid is added. The ether layer is separated, the aqueous layer is extracted

with ether, the solvent is distilled off from the combined ethereal solutions, and the residue is shaken for 3 hrs. with 20 ml of 1% hydrochloric acid. The product is extracted with ether, the extract is dried with anhydrous sodium sulfate, ether is distilled off, and the residue is vacuum distilled, giving 4.8 g of 6-keto-1-hydroxy-1,9-dimethyldecalin (V), b.p. 118-120°/0.05 mm; n_D^{25} 1.5149.

Found %: C 74.1; H 10.2

$C_{13}H_{20}O_2$. Calculated %: C 73.5; H 10.2

Some of the product undergoes dehydration during the distillation, to afford the unsaturated ketone (VI).

Dehydration of 6-keto-1-hydroxy-1,9-dimethyldecalin (V)

3.5 g of the above product (V) is heated for about 1 hr. at 160-165°/100 mm with 1.8 g of powdered potassium bisulfate, until water ceases to distil over, when the pressure is reduced to 4 mm, at which the dehydration product is distilled over, giving 2.1 g of 6-keto-1,9-dimethyl- Δ^1 -octalin (VI), b.p. 104-108°/4 mm; n_D^{25} 1.5092.

Found %: C 81.14; 81.34; H 9.84; 9.97

$C_{12}H_{18}O$. Calculated %: C 80.99; H 10.11

The semicarbazone, m.p. 172-174°, was recrystallized from methanol.

Found %: N 17.69; 17.77

$C_{12}H_{18}ON_3$. Calculated %: N 17.8

Action of magnesium methyl iodide on 6-keto-1,9-dimethyl- Δ^1 -octalin (VI)

A solution of 3 g of 6-keto-1,9-dimethyl- Δ^1 -octalin (VI) in 10 ml of absolute ether was added drop by drop, with constant stirring, and cooling in ice, to a Grignard solution prepared from 0.6 g of magnesium and 5 g of methyl iodide in 40 ml of absolute ether. The mixture is left for 2 hrs at room temperature, and 20 ml of 1% hydrochloric acid is added, cooling in ice. The product is extracted with ether, and the extract is dried with anhydrous magnesium sulfate, the ether is distilled off, and the residue is fractionally distilled in vacuum, giving 2.6 g of 6-hydroxy-1,6,9-trimethyl- Δ^1 -octalin (VII), b.p. 100-105°/3 mm; n_D^{25} 1.5104.

Found %: C 80.18; 80.15; H 11.12; 11.25

$C_{13}H_{22}O$. Calculated %: C 80.41; H 11.34

Dehydration of 6-hydroxy-1,6,9-trimethyl- Δ^1 -octalin (VII)

A mixture of 2.9 g of 6-hydroxy-1,6,9-trimethyl- Δ^1 -octalin (VII) and 1.5 g of powdered potassium bisulfate was heated for 1 hr at 165-175°, and the resulting hydrocarbon was then distilled over in vacuum. After redistillation at the ordinary pressure, from metallic sodium, 1.4 g of 1,6,9-trimethyl- $\Delta^{1,6}$ -hexalin (XII), b.p. 229-231°; n_D^{25} 1.5035.

Found %: C 87.53; 87.41; H 11.47; 11.61

$C_{13}H_{20}$. Calculated %: C 88.57; H 11.43

Dehydrogenation of 1,6,9-trimethyl- $\Delta^{1,6}$ -hexalin (XII)

1 g of the hydrocarbon (XII) was vaporized, and the vapor was passed during 2 hrs through a glass tube filled with palladized charcoal (tube length 40 cm, diameter 0.5 cm; 5% Pd in catalyst,) at 330-340°, regulating the rate of flow of the vapor according to the rate of evolution of hydrogen. Fractional distillation of the distillate gave a hydrocarbon of b.p. 130-133°/13 mm; n_D^{25} 1.6078, the picrate of which melted at 108-110° (recrystallized from methanol), and did not depress the m.p. of the picrate of a known specimen of 1,6-dimethylnaphthalene [3].

Action of magnesium methyl iodide on 1,6-diketo-9-methyldecalin (IX)

A solution of 3 g of 1,6-diketo-9-methyldecalin (IX) in 30 ml of absolute ether is added drop by drop, with constant stirring, and cooling in ice, to Grignard reagent prepared from 1.2 g of magnesium and 7.5 g of methyl iodide in 20 ml of absolute ether, after which the mixture is boiled for 3 hrs under reflux, and 20 ml of 1% hydrochloric acid is added to the solution of 0°. The solution is extracted with ether, the ethereal extract is dried with magnesium sulfate, the solvent is distilled off, and the residue is vacuum distilled, giving 3.2 g of 1,6-dihydroxy-1,6,9-trimethyldecalin (X), b.p. 113-116°/0.05 mm; n_D^{25} 1.5115.

Found %: C 73.34; 73.32; H 11.01; 10.97

$C_{13}H_{24}O_2$. Calculated %: C 73.59; H 11.32

Dehydration of 1,6-dihydroxy-1,6,9-trimethyldecalin (X) and dehydrogenation of mixtures of hydrocarbon (XII) and oxide (XI)

A mixture of 4 g of 1,6-dihydroxy-1,6,9-trimethyldecalin (X) and 2 g of potassium bisulfate powder was heated at 150-155°/100 mm, until evolution of water ceased (1 hr). The residue was extracted with ether, and the extract was dried, and distilled from sodium, giving 2.8 g of colorless liquid, b.p. 110-112°/19 mm; n_D^{20} 1.4977.

Found %: C 83.75; 83.59; H 11.41; 11.43
C₁₈H₃₀. Calculated %: C 88.57; H 11.43
C₁₈H₂₂O. Calculated %: C 80.35; H 11.41

The product appears to be a mixture of 1,6,9-trimethyl- $\Delta^{1,6}$ -hexalin (XII) with the corresponding oxide (XI).

Dehydrogenation of 3 g of the mixture under the conditions described above gave 0.7 g of 1,6-dimethylnaphthalene, b.p. 126-128°/10 mm; n_D^{20} 1.6078, picrate, m.p. 108-110° (from methanol), not depressing the m.p. of the picrate of a known specimen of 1,6-dimethylnaphthalene, prepared by a published method from β -ionone, and having m.p. 128-130° at 12 mm; n_D^{20} 1.6083, m.p. of picrate 107-109° [3].

Condensation of 2-methoxybuta-1,3-diene with methyl methacrylate

A mixture of 4 g of 2-methoxybuta-1,3-diene (b.p. 74-75°; n_D^{20} 1.4438) 4.8 g of methyl methacrylate (b.p. 99-100°; n_D^{20} 1.4150), and 0.1 g of pyrogallol in 9 g of dry benzene was heated at 219-220° in a metal tube for 3 hrs, the solvent was distilled off, and the residue was vacuum distilled, giving 5.2 g of 1-carbomethoxy-4-methoxy-1-methylcyclohex-3-ene (XIII), b.p. 107-108°/12 mm; n_D^{20} 1.4722

Found %: C 65.04; 65.32; H 8.98; 8.76
C₁₀H₁₆O₂. Calculated %: C 65.22; H 8.69

Preparation of 1-carbomethoxy-4-keto-1-methylcyclohexane (XIV)

5 g of 1-carbomethoxy-4-methoxy-1-methylcyclohex-3-ene (XIII) was shaken with 25 ml of 1% hydrochloric acid for 4 hrs at room temperature, the product was extracted with ether, the extract was dried with sodium sulfate, and distilled in vacuum, giving 3 g of 1-carbomethoxy-1-methylcyclohexan-4-one (XIV), b.p. 99-101°/7 mm; n_D^{20} 1.4610

Found %: C 63.63; 63.92; H 8.69; 8.35
C₉H₁₄O₂. Calculated %: C 63.53; H 8.23

The semicarbazone melts at 166-168°, after recrystallization from methanol, and gives no depression with the semicarbazone of a known specimen of the ester [4]; similar results are obtained with the 2,4-dinitrophenylhydrazone, m.p. 125-127° (from benzene), which gives no depression with a known specimen [4].

Preparation of 1-methylcyclohexan-4-one-1-carboxylic acid (XV)

A mixture of 2 g of 1-carbomethoxy-1-methylcyclohexan-4-one (XIV) 6 ml of glacial acetic acid, 1.5 ml of concentrated hydrochloric acid, and 0.9 ml of water was boiled for 6 hrs, volatile products were distilled off, and the residue was distilled in vacuum giving 1-methylcyclohexan-4-one-1-carboxylic acid (XV), b.p. 145-148°/2 mm; m.p. 77-78° (from benzene).

Found %: C 61.32; 61.19; H 7.78; 7.73
C₈H₁₂O₂. Calculated %: C 61.54; H 7.69

The m.p. of a known specimen of the acid was not depressed by admixture with our product [4].

1,3-Dicarbomethoxy-1-methylcyclohexan-4-one (XVII)

This ester, b.p. 130-132°/3 mm, n_D^{20} 1.4859, was prepared by the standard method of cyclization of 1,3,5-tricarbomethoxy-3-methyl-n-pentane (XVI) [4].

Hydrolysis of 1,3-dicarbomethoxy-1-methylcyclohexane-4-one (XVII)

5 g of the ester (XVII) was shaken with 40 ml of 5% caustic soda until it dissolved (2-3 min), and the solution was made acid after 8 hrs at room temperature, with dilute (1:1) hydrochloric acid, when 3.7 g of

1-methylcyclohexan-4-one-1:3-dicarboxylic acid (XVIII), m.p. 104-106° (decomp.) separates out.

Found: Equiv. titration 99.3.

$C_9H_{12}O_4$. Calculated: Equiv. titration 100.0.

Decarboxylation of 1-methylcyclohexan-4-one-1:3-dicarboxylic acid (XVIII)

3.7 g of the acid (XVIII) was heated for 1 hour at 120°, until evolution of carbon dioxide ceased, and the residue was recrystallized from petroleum ether, giving 2.3 g of 1-methylcyclohexan-4-one-1-carboxylic acid (XV), m.p. 76-78°, not depressing the m.p. of a specimen of this acid prepared by diene condensation with the ester (XIII).

Esterification of 1-methylcyclohexan-4-one-1-carboxylic acid (XV)

5 g of the acid (XV) is added gradually, with stirring, to 250 ml of an ethereal solution of diazomethane, prepared from 25 g of nitrosomethylurea, the ether is distilled off, and the residue is distilled in vacuum, giving 4.2 g of 1-carbomethoxy-1-methylcyclohexan-4-one (XIV), b.p. 115-117°/14 mm., n_D^{20} 1.4612 [4].

The semicarbazone, m.p. 168-169°, and the 2:4-dinitrophenylhydrazone, m.p. 127-128°, did not depress the m.p. of the corresponding derivatives of the keto-ester (XIV) prepared by diene condensation of the ester (XIII).

Preparation of 1-carbomethoxy-1-methylcyclohex-2-en-4-one (XXI)

A solution of 8.4 g of dry bromine in 20 g of carbon tetrachloride was added drop by drop, with constant stirring and cooling in ice, to 10 g of 1-carbomethoxy-4-methoxy-1-methylcyclohex-3-ene (XIII) in 30 g of carbon tetrachloride. The solution was then shaken for 15 min. with 62 ml of water, and the lower layer was separated, dried with sodium sulfate, and evaporated down in vacuum. The bromo-ester (XX) so obtained was heated for 1 hour at 150-155° with 9.5 g of dry diethylaniline, and the crystalline product obtained on cooling was treated with dilute (1:1) hydrochloric acid. The product was extracted with benzene, the extract was dried with sodium sulfate, and distilled in vacuum, giving 4 g of 1-carbomethoxy-1-methylcyclohex-2-en-4-one (XXI), b.p. 107-110°/7 mm., n_D^{20} 1.4775 [4]. The semicarbazone melted at 157-158°, after recrystallization from methanol.

Found %: N 18.8; 18.6

$C_{10}H_{14}O_3N_2$. Calculated %: N 18.7

Condensation of 1-carbomethoxy-1-methylcyclohex-2-en-4-one (XXI) with malonic ester

4 g of 1-carbomethoxy-1-methylcyclohex-2-en-4-one (XXI) is added during 10 min., with stirring, to a solution of sodium-malonic ester prepared from 15 g of malonic ester and 0.54 of sodium, and the mixture is heated at 70-76° for 7 hours. The cooled solution is made acid at 0° with dilute (1:1) hydrochloric acid, the product is extracted with benzene, the extract is dried with sodium sulfate, and distilled in vacuum, giving 2.2 g of the tricarboxylic ester (XXII), b.p. 155-157°/1.5 mm., n_D^{20} 1.4888.

Found %: C 58.77; 58.91; H 6.62; 6.75

$C_{16}H_{24}O_7$. Calculated %: C 58.60; H 7.30

SUMMARY

Condensation of 2-methoxybuta-1:3-diene with 1-methylcyclohex-1-en-6-one and methyl methacrylate gives the p-substituted products (III) and (XIII), the structure of which was established by converting them into the known compounds (VIII) and (XV), which were also synthesized by standard methods, for their identification.

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Academy of Sciences, U.S.S.R.

* See Consultants Bureau English translation, pages 685, 697, 911.

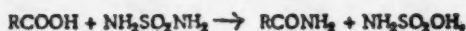
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NEW DATA ON THE CHEMISTRY OF AMIDES OF SULFURIC ACID AND TRICHLOROPHOSPHAZOSULFONARYLS*

A. V. Kirsanov

I. Mechanism of Amidation of Carboxylic Acids with Amides of Sulfuric Acid.

It is known that carboxylic acids react with sulfamides to give amides in almost quantitative yield [1] by the reaction:



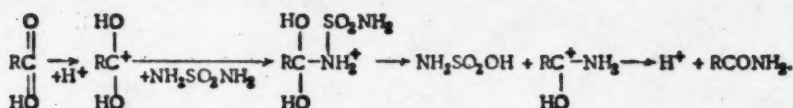
With asymmetrical dimethylsulfamides, only dimethylamides are obtained, by the reaction [2]:



Symmetrical diphenylsulfamides give anilides of the appropriate acids, by the reaction:

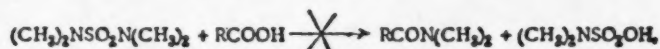


These reactions may be explained by a mechanism analogous to that of esterification [1], i.e.:



If this mechanism is in fact applicable, it must follow that any sulfamide should be capable of amidating carboxylic acids, including tri- and tetra-substituted sulfamides; the presence of a "free" hydrogen atom in the sulfamide molecule is not essential.

An experimental study of the reaction of amidation of carboxylic acids (acetic and benzoic) with tetra-substituted sulfamides (tetramethyl- and symmetrical diphenyldimethyl- and diphenyldiethyl-sulfamide) showed that the reaction:

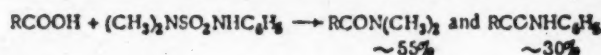


does not take place, the sulfamides being recovered unreacted in amounts of 99.1–99.4%, and the benzoic acid in amounts of 97.8–98.5%, in a pure state. It follows that the proposed mechanism cannot be the correct one.

It is evident that the presence within the sulfamide molecule of "free" hydrogen atoms is essential for the amidation reaction, and that such "free" atoms (or atom) must enter into the reaction mechanism. In order to ascertain whether there must be one or two "free" hydrogen atoms in the sulfamide molecule a study was made of the reaction between tri-substituted sulfamides and carboxylic acids (trimethylsulfamide and asymmetrical phenyldimethylsulfamide with benzoic and p-nitrobenzoic acid). The reaction proceeded smoothly; only the dimethylamide of the carboxylic acid was obtained with trimethylsulfamide, as follows:



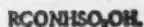
With phenyldimethylsulfamide the products are dimethylamide and anilide, by the reaction:



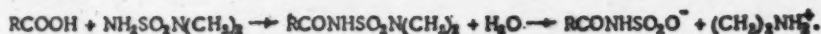
* Read at a general meeting of the Division of Chemical Sciences of the Academy of Sciences, U.S.S.R. on March 27, 1952.

It follows that it is sufficient for the reaction of amidation that the sulfamide should contain at least one "free" hydrogen atom, i.e., all except tetra-substituted sulfamides can be used for amidation.

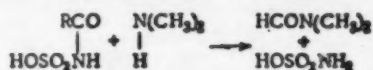
The definite conclusion may be drawn that intermediate products of the reaction must be either acylsulfamides or acylsulfamic acids:



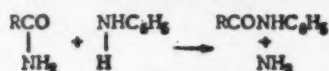
At first sight, however, it then appears inexplicable how dialkylamides can be formed. It seems that hydrolysis of acylsulfamides can give only amides or monoalkylamides. These contradictions appeared for a long time to be irreconcilable, but the explanation was eventually found. Apparently the water formed in the production of acylsulfamide hydrolyzes the "free" amino-group of acylsulfamide, giving the ammonium salt of acylsulfamic acid, as follows:



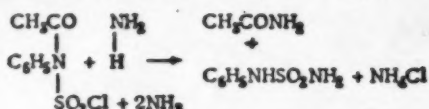
The action of pyridine on the salt gives free ammonia or amine, which causes aminolysis of the C-N bond, with formation of amide, monosubstituted amide, or disubstituted amide, by the reaction:



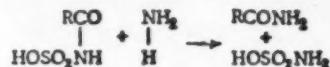
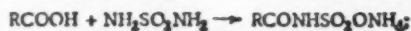
Analogous cases of aminolysis are known, such as the reaction of trans-amination of carboxylic acids [3]:



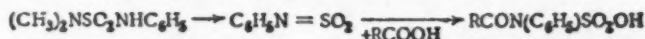
and the aminolysis of chlorides of arylacysulfamic acids [4]:



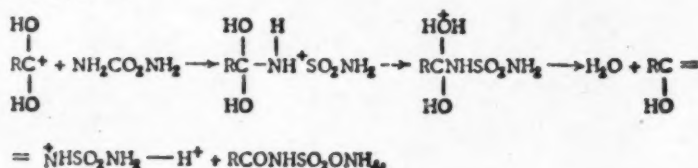
It is thus quite likely that acylsulfamic acids are in fact intermediate products of the reaction of amidation, which would thus proceed as follows:



Acylsulfamic acids may be formed in two ways; either isosulfamic acid is formed as an intermediate product, i.e., the reaction proceeds as follows:



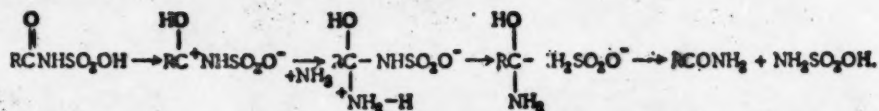
or, as is more probable, the reaction mechanism is analogous to that of esterification, but differs in certain respects from that previously proposed:



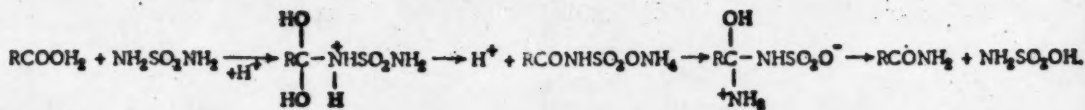
i.e., the product of addition of sulfamide to the active complex of the acid eliminates water, and not sulfamic acid, in the same way as in the reaction of esterification. This reaction scheme is thus far closer to that of esterification than was the original, incorrect scheme.

It is quite possible that pyridine takes part in the amidation reaction, which either does not proceed at all in its absence, or does so only at higher temperatures, giving low yields. Numerous attempts have been made to isolate intermediate products containing pyridine, without any success; these products are evidently highly

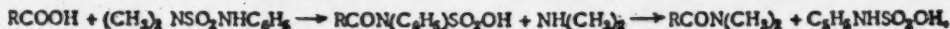
unstable, and enter into further reaction as soon as they are formed. It is probable that the product of addition of pyridine to sulfamide is formed first, possibly being of the type of a betainopyridonium salt of sulfamic acid, and the sulfamide so activated then reacts with the carboxylic acid according to the above scheme; formation of imidosulfamide in the reaction of pyridine with sulfamide has been thus explained [5], and aminolysis may take place in the same way, i.e.,



It is thus very probable that the reaction of amidation of carboxylic acids by sulfamides proceeds according to the following mechanism:



This reaction mechanism explains all the observed facts except one. If it is the correct mechanism, we should expect to obtain only dimethylamides from phenyldimethylsulfamide and carboxylic acids, by the scheme:

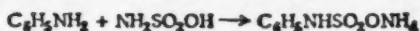


whereas in fact we obtain a mixture of dimethylamides and anilides. This may mean that the proposed mechanism is not the actual one, or that some other, additional factors enter into the picture. Examination of the above scheme shows that it differs basically from the general one for unsubstituted sulfamides. In the reaction between carboxylic acids and unsubstituted or asymmetrically disubstituted sulfamides stable, difficultly hydrolyzable sulfamic acid is obtained as a by-product, whereas with phenyldimethylsulfamide the by-product is unstable, very readily hydrolyzable phenylsulfamic acid. This acid gives stable salts, but it is so unstable in the free state that it has never yet been isolated. Two authors who claim to have done so give melting points of 77° [6] and over 280° [7]. The acid tends to undergo hydrolysis at the nitrogen-sulfur bond, so that there is strong reason to believe that carboxylic acids should cause acidolysis of phenylsulfamic acid, as follows:



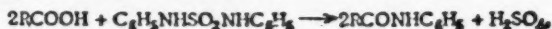
i.e., with formation of anilides. This supposition was confirmed by experiment.

Ammonium phenylsulfamate was prepared from sulfamic acid and aniline by the reaction:



and was heated, without prior purification, with p-nitrobenzoic acid in pyridine solution, giving the corresponding anilide in ~30% yield; this confirms the accuracy of our theoretical supposition, and also gives us a new method for the direct conversion of carboxylic acids into their anilides. It is possible that this method may be adopted in practice, since arylsulfamic acids are readily available as their ammonium salts.

Formation of anilides from phenylsulfamic acid and carboxylic acids was also confirmed by another experiment, in which 2 g-mols. of p-nitrobenzoic acid in pyridine was heated with 1 g-mol. of phenylsulfamide, giving p-nitrobenzanilide in 73.0% yield, by the reaction:



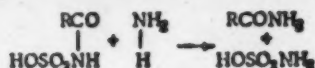
or in 147.2% yield by the reaction:



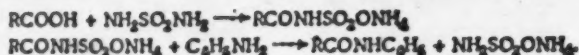
This can only be explained on the assumption that the carboxylic acid acidolyzes phenylsulfamic acid, giving phenylsulfamide. Unsubstituted sulfamic acid and alkylsulfamic acids do not under such conditions react with carboxylic acids.

The reaction mechanism presented by us for the reaction of amidation is thus in conformity with all the observed facts. However, a theory should not only explain all the known facts; it should also predict as yet unknown ones. Let us see what our theory predicts, and how the predictions are confirmed by experiment.

The second stage of the reaction consists of aminolysis of acylsulfamic acids:

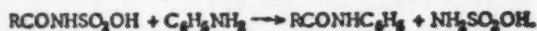


The first conclusion to be derived is hence that if the reaction of amidation is performed with an unsubstituted sulfamide, but in the presence of an "outside" amine, a substituted amide should be obtained, e.g.:



This was confirmed for the case sulfamide - *p*-nitrobenzoic acid - aniline. The yields, calculated on reacted *p*-nitrobenzoic acid, were: anilide ~58%, unsubstituted amide ~30% of theory.

A second deduction is that the ammonia (or amides) should react with acylsulfamic acids to give amides (or substituted amides) of carboxylic acids and sulfamic acids:



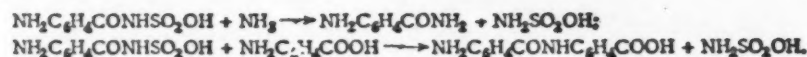
Pyridonium benzoylsulfamate was prepared by heating a mixture of benzamide and betainopyridonium sulfamate, and the reaction product (without separating benzoylsulfamate) was heated with aniline, giving ~70% yield of benzanilide, calculated on reacted benzamide. Our second deduction is thus confirmed.

Acylsulfamic acids have up to now been little studied, but there is reason to believe that they may become cheap and readily available substances, in which case this reaction may become of commercial interest.

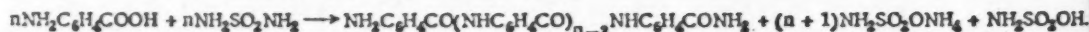
A third deduction is that polypeptides should be obtained by the action of sulfamides on amino-acids. Thus *p*-aminobenzoylsulfamic acid should be obtained as an intermediate product in the reaction between sulfamide and *p*-aminobenzoic acid:



This product may then undergo aminolysis at the carbon-nitrogen bond when treated with ammonia, to give *p*-aminobenzamide, or, by reaction with the amino-group of *p*-aminobenzoic acid, it may give the dipeptide of aminobenzoic acid, as follows:



Of these two, the second reaction should be the faster one, since the amino-group is, at least initially, present in greater concentration than the ammonia, especially if free ammonia enters into the reaction, having been displaced from the salt by pyridine. But if dipeptide is formed there is no reason to suppose that the same process will not go further, to give tripeptide, tetrapeptide, and so on.



Only experiment can show which will be the final product formed by this process. The degree of condensation will obviously depend on the solubility of the polypeptides in the reaction medium and on the experimental conditions in general.

All these theoretical conclusions emerging from our proposed reaction mechanism were confirmed experimentally. The action of sulfamide on *p*-aminobenzoic acid in pyridine solution, at temperatures not greater than 100°, i.e., under the ordinary amidation conditions, gives a mixture of polypeptides of *p*-aminobenzoic acid, in good yield. The main product is a colorless, infusible mass of polypeptides, insoluble in the usual organic solvents. As was to be expected, no *p*-amino-benzamide was obtained. Amidation and phenylamidation of *p*-dimethylaminobenzoic acid, however, gave good yields of *p*-dimethylaminobenzamide- or -benzanilide, as would follow from our theory.

It would have been of very great interest to prepare polypeptides in the same way from aliphatic amino-acids, but this could not be realized, because of the insolubility in pyridine of the simpler amino-acids, such as alanine or glycine, which cannot thus be made to react with sulfamides.

The reaction mechanism proposed by us for amidation of carboxylic acids with sulfamides not only gives a satisfactory explanation of all the known reactions, but has led to the finding of further applications of this re-

action, such as the finding of a new variant, that of preparation of anilides by reaction with phenylsulfamic acid. Our mechanism also allowed us to predict the effect of adding another amine to the reaction systems, to predict that acylsulfamic acids should give amides with amines, and that amino-acids soluble in pyridine should give polypeptides instead of amides in the conditions of the reaction.

II. New Method of Preparation of Trichlorophosphazosulfonyls

Trichlorophosphazosulfonyls are, as is known, prepared by the action of phosphorus pentachloride on sulfonamides [9]. This method is very convenient for the trichloro-derivatives, and it might conceivably be extended to tribromophosphazosulfonyls, but it certainly could not be applied to preparation of trifluorophosphazosulfonyls or of azosulfonyls.

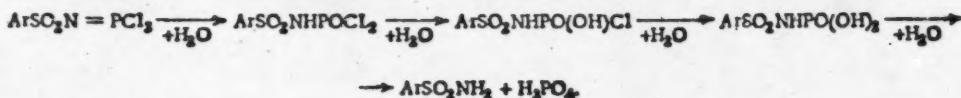
The limitations of this method led us to seek for a new method of a more general nature, applicable to preparation of analogs of trichlorophosphazosulfonyls: in which both the halogen and the phosphorus are replaced by other elements. Such a method was recently found; it depends on the action of alkali metal salts of sulfochloramides: on phosphorus trichloride, by the reaction:



which proceeds smoothly, giving practically quantitative yields. Substitution of phosphorus tribromide for trichloride gives the corresponding tribromo-derivative, and of arsenious for phosphorus trichloride the corresponding arsenic compound.

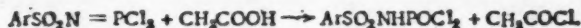
III. Hydrolysis and Aminolysis of Trichlorophosphazosulfonyls

Hydrolysis of trichlorophosphazosulfonyls should proceed as follows:

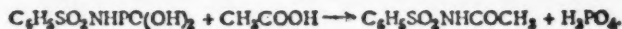


Hydrolysis was studied in solutions in acetone, ethers, and esters, and in all cases very difficultly separable mixtures were obtained, from which only very small yields of crystalline hydrolysis products were isolated. Satisfactory results were obtained by hydrolysis with steam in benzene solution, whereby were obtained the dichlorides of phenyl-, o-tolyl-, p-tolyl-, and 1-naphthyl-sulfonamidophosphoric acid in good yield.

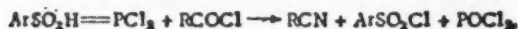
Since all attempts at obtaining products in which the second and third halogen atoms have undergone hydrolysis were unsuccessful, we decided to apply acidolysis instead of hydrolysis, in the expectation that this would give the same products as would have hydrolysis, with the difference that the by-product would be the acid chloride instead of hydrogen chloride, as follows:



Apart from this the final product of acidolysis should be acylsulfamide instead of sulfamide, such as:



Experiments performed with acetic and benzoic acids showed, however, that it is not possible to use any acid in order to achieve all the intermediate degrees of acidolysis. The acid chlorides formed as byproducts react with trichlorophosphazosulfonyls when heated, giving cyanides and arylsulfochlorides [10], as follows:



which greatly complicates the isolation in a pure state of acidolysis products.

It was therefore necessary to find an acid which would not give rise to undesirable by-products; formic acid should theoretically be suitable, as its chloride decomposes as soon as it is formed, giving hydrogen chloride and carbon monoxide. This was confirmed experimentally, all stages of hydrolysis being obtained in good yield, viz., arylsulfonamidophosphoric acid, and its mono- and di-chlorides. In general, formic acid may be recommended as an excellent reagent for conversion of acid chlorides into the free acids.

Experiments on acidolysis were performed on five trichlorophosphazosulfonyls (phenyl, o- and p-tolyl,

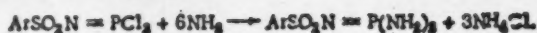
E. A. Abrazhanova's experiments.

and 1- and 2-naphthyl), using three acids (formic, acetic and benzoic). With acetic and benzoic acid only products of the first degree of hydrolysis were obtained in good yield. All the intermediate products of hydrolysis of trichlorophosphazosulfonyls are crystalline substances, fairly readily hydrolyzable, and readily entering into reaction with alcohols, phenols, and aromatic and aliphatic amines. Some of them have an extremely bitter taste. They are all only very slightly toxic.

Acidolysis of arylsulfonamidophosphoric acids gives sulfamides, together with acylsulfamides; this is due to thermal decomposition of the acids, as follows:

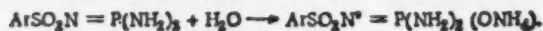


Ammonia reacts with trichlorophosphazosulfonyls to give triamides of arylsulfonimidophosphoric acids (triaminophosphazosulfonyls), as follows:

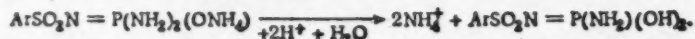


These are crystalline substances, fairly soluble in water.

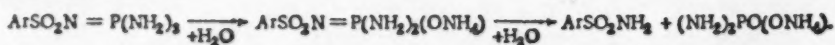
The triamides of arylsulfonamidophosphoric acids appear to be the first compounds described in which a phosphorus atom is joined to four atoms of nitrogen. Aqueous solutions of triamides have a neutral reaction, and cannot be titrated with phenolphthalein indicator, but the triamides gives mono-silver salts. They are fairly quickly hydrolyzed in aqueous solution, giving ammonium salts of diamidoarylsulfonimidophosphoric acids, as follows:



These ammonium salts are converted by the action of silver nitrate solution into the corresponding silver salts, which are colorless, finely crystalline substances, sparingly soluble in water. The free acids could not be obtained, as when the solutions of their salts were made acid hydrolysis of another amino-group took place, giving monoamidoarylsulfonamidophosphoric acid, as follows:



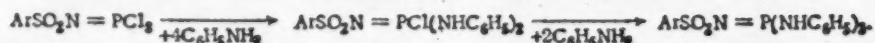
When aqueous solutions of triamides (not acidified) are boiled, sulfamides and ammonium diamidophosphate are formed, by the reactions:



Free diamidoarylsulfonamidophosphoric acids thus readily undergo hydrolysis at the phosphorus - amino-group bond, whereas salts of diamidophosphoric acids are hydrolysed at the phosphorus - arylsulfonamido-group bond.

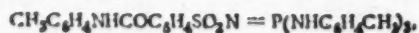
Only the monoamides of arylsulfonamidophosphoric acids were obtained by the action of ammonia on dichlorides of arylsulfonamidophosphoric acids; for this reason the diamides of arylsulfonamidophosphoric acids have not yet been prepared; the monoamides always being obtained. The monoamides of arylsulfonamidophosphoric acids are most conveniently prepared by the action of aqueous ammonia on trichlorophosphazosulfonyls or on the dichlorides of arylsulfonamidophosphoric acids; they are crystalline, acidic substances, titratable as dibasic acids, and readily hydrolyzed in boiling aqueous solution.

Aromatic amines react with trichlorophosphazosulfonyls as follows:



This reaction was studied in the cases of four different trichlorophosphazosulfonyls (phenyl, o-tolyl, p-tolyl, and 1-naphthyl) and two amines (aniline and p-toluidine). The products of the first stage of the process, viz., the monochlorides of dianilidoarylsulfonimidophosphoric acids, are crystalline substances, readily hydrolyzable to the corresponding acids. The free dianilidoarylsulfonamidophosphoric acids behave as monobasic acids, and do not undergo hydrolysis in aqueous solutions even when these are heated. They are, however, readily hydrolyzed by boiling with strong mineral acids.

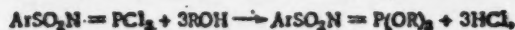
The final products of the reaction, viz., the trianilides of aryl-sulfonimidophosphoric acids, are neutral crystalline substances, insoluble in alkaline solutions, and not hydrolyzed when boiled with water. It is of interest that one of these trianilides has long been known, although its structure was not known; this is the trianilide of the structure:



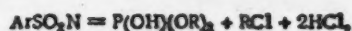
obtained by Rodionov and Yavorsky [8] in 1948 by the action of *p*-toluidine on the chloride of *p*-trichlorophosphazosulfobenzonic acid.

IV. Reaction of Trichlorophosphazosulfonyls with Alcohols and Phenols*

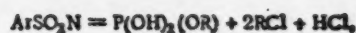
As was to be expected, trichlorophosphazosulfonyls react with alcohols similarly to phosphorus oxychloride, i.e., according to the experimental conditions they form either esters of arylsulfonamidophosphoric acid or alkyl halides and free arylsulfonamidophosphoric acids, or both processes may take place simultaneously. The reaction products should thus be: triesters of arylsulfonamidophosphoric acids, diesters of arylsulfonamidophosphoric acids, monoesters of arylsulfonamidophosphoric acids, and free arylsulfonamidophosphoric acids:



or



or

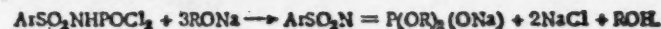


or



The triesters are formed together with diesters from trichlorophosphazosulfonyls and sodium alkoxide or phenoxide in alcoholic solution or in neutral solvents.

The diesters are obtained in almost quantitative yield by the action of sodium alkoxides on dichlorides of arylsulfonamidophosphoric acids, as follows:



The tri-methyl-, -ethyl-, -butyl-, -phenyl-, and -nitrophenyl esters of 1- and 2-naphthylsulfonamidophosphoric acid are crystalline substances of low melting point. The methyl and ethyl esters are slowly hydrolyzed by boiling aqueous alkalis, giving the diesters. The nitrophenyl esters are very readily hydrolyzed. The tri-methyl-, -ethyl-, and -butyl esters of phenyl- and *o*-tolyl-sulfonamidophosphoric acids are odorless low m.p. solids or liquids.

The di-methyl-, -ethyl-, -butyl-, -phenyl-, and -nitrophenyl esters of arylsulfonamidophosphoric acids are crystalline, very bitter substances, which can be titrated as monobasic acids with phenolphthalein indicator; they give crystalline salts. The sodium salt of dibutyl esters is soluble in benzene, and can be crystallized from petroleum ether.

SUMMARY

1. A scheme explaining the reactions of amidation of carboxylic acids by amides of sulfuric acid is presented, and is experimentally established.
2. It is shown that phenylsulfamic acid in pyridine solution reacts with carboxylic acids to give their anilides.
3. The product of reaction of amines with acylsulfamic acids is shown to be an acylamine.
4. The products of reaction of *p*-aminobenzonic acid with sulfamides are shown to be polypeptides of *p*-aminobenzonic acid.
5. A new method has been found for preparation of trihalogenophosphazosulfonyls, from alkali metal salts of chloramides of arylsulfonic acids and the appropriate phosphorus trihalides.
6. The hydrolysis and acidolysis of trichlorophosphazosulfonyls have been studied. All the theoretically possible intermediate and final products of hydrolysis and acidolysis of trichlorophosphazosulfonyls were obtained, viz., the mono- and di-chlorides of arylsulfonamidophosphoric acids, free arylsulfonamidophosphoric acids, and acylsulfamides.
7. The aminolysis and arylaminolysis of trichlorophosphazosulfonyls have been studied. The products are: triamides of arylsulfonamidophosphoric acids, salts of diamides of arylsulfonamidophosphoric acids, mono-amides of arylsulfonamidophosphoric acids, chlorides of dianilidoaryl-sulfonamidophosphoric acids, dianilides of

* V. I. Shevchenko's experiments.

arylsulfonamidophosphoric acids, and trianilides of arylsulfonimidophosphoric acids.

8. The reaction between trichlorophosphazonesulfonyls and alcohols or phenols has been studied. The products are triesters of arylsulfonimidophosphoric acids and diesters of arylsulfonamidophosphoric acids.

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Stalin Dnepropetrovsk Metallurgical Institute

- * See Consultants Bureau English Translation, p. a-675.
- ** See Consultants Bureau English Translation, p. 1273.
- *** See Consultants Bureau English Translation, p. 1713.
- **** See Consultants Bureau English Translation, p. 329.
- ***** See Consultants Bureau English Translation, p. 335.

NEW METHOD FOR SYNTHESIS OF PHOSPHINIC AND THIOPHOSPHINIC ACID ESTERS*

PART II. ADDITION OF DIALKYLPHOSPHOROUS ACIDS TO THE AMIDE AND ESTERS OF METHACRYLIC ACID

A. N. Pudovik and D. Kh. Yarmukhametova

It has been shown by one of us that a very simple method for the synthesis of phosphonocarboxylic acids is to add dialkylphosphorous acids to esters of unsaturated carboxylic acids. Addition of dimethyl-, diethyl-, dibutyl-, and diisobutyl-phosphorous acids to methyl acrylate [1], methyl methacrylate [2], ethyl crotonate, and ethyl cinnamate gave the esters of dialkylphosphone-propionic, -isobutyric, and -phenylpropionic acids, in quantitative yields. In this paper we shall describe the results of attempted addition of dialkylphosphorous acids to amides of unsaturated acids, of higher dialkylphosphorous acids to esters of $\alpha\beta$ -unsaturated acids, and of dialkylphosphorous acids to esters of unsaturated carboxylic acids with various alcohols. The experiments were done with the amide and esters of methacrylic acid.

Addition of dialkylphosphorous acids to the amide was effected in the presence of alkali metal alkoxides. The reaction proceeded quite energetically, with evolution of considerable heat, giving the amides of diethyl-, dipropyl-, and di-n-butyl-phosphoneisobutyric acid; the constants of the products, and their yields, are given in Table 1.

It appears from Table 1 that the yields are low, not exceeding 31% (ethyl ester). We were not able to pre-

TABLE 1

Serial No.	Formula	B.p. °C/p in mm	n_D^{20}	D_4^{20}	Yield %
1	$(C_2H_5O)_2P(=O)CH_2CH(CH_3)CONH_2$	146-147/13	1.4361	1.0624	31
2	$(n-C_4H_9O)_2P(=O)CH_2CH(CH_3)CONH_2$	164-165/12	1.4421	0.9941	15
3	$(n-C_3H_7O)_2P(=O)CH_2CH(CH_3)CONH_2$	135°/2	1.4438	1.0437	17

pare the product of addition of dimethylphosphorous acid to methacrylamide, as it decomposed when distilled. Addition of dihexyl-, diheptyl-, and dioctyl-phosphorous acid to methyl methacrylate was next studied; the reaction proceeds fairly readily, with evolution of heat, but the yields were much lower than with lower mol. wt. dialkylphosphorous acids. The constants of the products obtained are given in Table 2.

Finally, addition of diethylphosphorous acid to alkyl methacrylates (the alkyl being ethyl to octyl) was studied; the reaction proceeds energetically in most cases. The constants and yields of the products are given in Table 3, from which it appears that the yields are lower than with methyl methacrylate (74.5%).

EXPERIMENTAL

Addition of Diethylphosphorous Acid to Methacrylamide

A concentrated solution of sodium ethoxide in absolute ethanol was added gradually to 8 g of diethylphosphorous acid and 5 g of methacrylamide in an Arbuzov flask. The reaction proceeds energetically, with considerable

* This and succeeding papers are parts of a series having the general title "Addition of dialkylphosphorous acids to unsaturated compounds," published in the Journal of General Chemistry during the past two years. The change in the general title is due to the circumstance that the new synthesis of esters of phosphorous acid discovered by us was originally based on addition of dialkylphosphorous acids to unsaturated electrophilic reagents, but has now been extended to certain saturated compounds, and to esters of other types of acids derived from phosphorus.

TABLE 2

Serial No.	Formula	B.p. °C/p in mm	n_D^{20}	d_4^{20}	Yield %
1	$(n-C_6H_{13}O)_2P(=O)-CH_2-\overset{\overset{CH_3}{ }}{CH}-COOCH_3$	188-189/4	1.4442	0.9900	20
2	$(n-C_7H_{15}O)_2P(=O)-CH_2-\overset{\overset{CH_3}{ }}{CH}-COOCH_3$	183-185/1	1.4480	0.9653	14
3	$(n-C_8H_{17}O)_2P(=O)-CH_2-\overset{\overset{CH_3}{ }}{CH}-COOCH_3$	183-194/1	1.4489	0.9461	16

evolution of heat after the addition of each drop, initially. Further addition of ethoxide is discontinued when heat is no longer evolved (usually after the 8-10th drop), and the mixture is then heated at 100° for 2 hours, after which it is fractionally distilled, giving 3.5 g of β -diethylphosphonoisobutyramide (Table 1, compound 1). The

residue in the distilling flask was a tarry mass.

Found % P 13.8; 13.8
 $C_8H_{18}O_4NP$. Calculated % P 13.9

Addition of dipropylphosphorous acid to methacrylamide

7.8 g of dipropylphosphorous acid and 4 g of methacrylamide with sodium propoxide gave 2 g of β -dipropylphosphonoisobutyramide (Table 1, compound 2). Partial decomposition of the reaction product took place during distillation.

Found %: P 12.9
 $C_{12}H_{22}O_4NP$.
 Calculated %: P 12.4

Addition of dibutylphosphorous acid to methacrylamide

9 g of dibutylphosphorous acid and 4 g of methacrylamide with sodium butoxide gave 2.4 g of β -dibutylphosphonoisobutyramide (Table 1, compound 3).

Found %: P 11.0;
 10.80. $C_{12}H_{24}O_4NP$.
 Calculated %: P 11.1

TABLE 3

Serial No.	Formula	B.p. °C/p in mm	n_D^{20}	d_4^{20}	Yield %
1	$(C_2H_5O)_2P(=O)-CH_2-\overset{\overset{CH_3}{ }}{CH}-COOC_2H_5$	119-119.5/4	1.4339	1.0786	53
2	$(C_2H_5O)_2P(=O)-CH_2-\overset{\overset{CH_3}{ }}{CH}-COOC_2H_7(n)$	125-126/4	1.4342	1.0698	69
3	$(C_2H_5O)_2P(=O)-CH_2-\overset{\overset{CH_3}{ }}{CH}-COOC_2H_7(iso)$	113-114/4	1.4330	1.0797	59
4	$(C_2H_5O)_2P(=O)-CH_2-\overset{\overset{CH_3}{ }}{CH}-COOC_4H_9(n)$	140-142/4	1.4362	1.0508	44
5	$(C_2H_5O)_2P(=O)-CH_2-\overset{\overset{CH_3}{ }}{CH}-COOC_4H_9(iso)$	135-136/4	1.4362	1.0510	51
6	$(C_2H_5O)_2P(=O)-CH_2-\overset{\overset{CH_3}{ }}{CH}-COOC_8H_{17}(n)$	147-148/4	1.4392	1.0467	26
7	$(C_2H_5O)_2P(=O)-CH_2-\overset{\overset{CH_3}{ }}{CH}-COOC_7H_{15}(n)$	158-160/2.5	1.4410	1.0107	19
8	$(C_2H_5O)_2P(=O)-CH_2-\overset{\overset{CH_3}{ }}{CH}-COOC_8H_{17}(n)$	163-164/2.5	1.4419	1.0010	25
9	$(C_2H_5O)_2P(=O)-CH_2-\overset{\overset{CH_3}{ }}{CH}-COOC_9H_{19}(n)$	169-170/2.5	1.4421	0.9932	9
10	$(C_2H_5O)_2P(=O)-CH_2-\overset{\overset{CH_3}{ }}{CH}-COOCH_2-CH=CH_2$	117-119/2.5	1.4396	1.0799	41

Addition of dihexylphosphorous acid to methyl methacrylate

A solution (not saturated) of sodium hexoxide in hexanol was added gradually to 12.5 g of dihexylphosphorous acid and 5 g of methyl methacrylate, in an Arbuzov flask. Addition of sodium hexoxide was initially followed by evolution of heat, which no longer occurred after about 15 drops had been added. The mixture was then heated at 100° for 2 hours, and fractionally distilled, giving 3.3 g of methyl β -dihexylphosphonoisobutyrate (Table 2, compound 1).

Found %: P 8.9; 9.2

$C_{11}H_{25}O_5P$. Calculated %: P 8.9

Addition of diheptylphosphorous acid to methyl methacrylate

15 g of diheptylphosphorous acid and 5.4 g of methyl methacrylate with sodium heptoxide gave 2.5 g of methyl β -diheptylphosphonoisobutyrate.

Found %: P 7.7; 7.5

$C_{19}H_{39}O_5P$. Calculated %: P 8.2

Addition of dioctylphosphorous acid to methyl methacrylate

10 g of dioctylphosphorous acid and 3.3 g of methyl methacrylate with sodium octoxide gave 2.5 g of methyl β -dioctylphosphonoisobutyrate (Table 2, compound 3).

Found %: P 7.6; 7.5

$C_{21}H_{43}O_5P$. Calculated %: P 7.6

Addition of diethylphosphorous acid to esters of methacrylic acid

The esters used were prepared by trans-esterification of methyl methacrylate.

Ethyl methacrylate. Sodium ethoxide was added very gradually to 8 g of ethyl methacrylate and 9.7 g of diethylphosphorous acid, about 10 drops being added in all. Distillation of the reaction mixture gave 9.4 g of ethyl β -diethylphosphonoisobutyrate (Table 3, compound 1).

Found %: P 12.4; 12.1

$C_{10}H_{22}O_5P$. Calculated %: P 12.3

Propyl methacrylate. 7 g of propyl methacrylate and 7.7 g of diethylphosphorous acid similarly gave 10.2 g of propyl β -diethylphosphonoisobutyrate (Table 3, compound 2).

Found %: P 11.5; 11.6

$C_{11}H_{22}O_5P$. Calculated %: P 11.6

Isopropyl methacrylate. 7 g of isopropyl methacrylate and 7.6 g of diethylphosphorous acid gave 8.5 g of isopropyl β -diethylphosphonoisobutyrate (Table 3, compound 3).

Found %: P 11.3; 11.7

$C_{11}H_{22}O_5P$. Calculated %: P 11.6

Butyl methacrylate. 8 g of butyl methacrylate and 8 g of diethylphosphorous acid gave 6.9 g of butyl β -diethylphosphonoisobutyrate (Table 3, compound 4).

Found %: P 10.9; 10.9

$C_{13}H_{26}O_5P$. Calculated %: P 11.1

Isobutyl methacrylate. 6.2 g of diethylphosphorous acid and 6.2 g of isobutyl methacrylate gave 5.8 g of isobutyl β -diethylphosphonoisobutyrate (Table 3, compound 5).

Found %: P 11.5; 11.6

$C_{13}H_{26}O_5P$. Calculated %: P 11.1

Hexyl methacrylate. 8 g of diethylphosphorous acid and 9 g of hexyl methacrylate gave 2.3 g of hexyl β -diethylphosphonoisobutyrate (Table 3, compound 6).

Found %: P 10.3

$C_{14}H_{28}O_5P$. Calculated %: P 10.1

Heptyl methacrylate. 6 g of diethylphosphorous acid and 8 g of heptyl methacrylate gave 3.6 g of heptyl β -diethylphosphonoisobutyrate (Table 3, compound 7).

Found %: P 9.7; 9.6

$C_{15}H_{31}O_5P$. Calculated %: P 9.9

Octyl methacrylate. 7 g of diethylphosphorous acid and 10 g of octyl methacrylate gave 4.5 g of octyl

β -diethylphosphonobutyrate (Table 3, compound 8)

Found % P 8.8

$C_{18}H_{32}O_5P$. Calculated % P 9.2

Nonyl methacrylate. 6.2 g of diethylphosphorous acid and 10 g of nonyl methacrylate gave 2.4 g of nonyl β -diethylphosphonobutyrate (Table 3, compound 9).

Found % P 8.9; 8.5

$C_{17}H_{30}O_5P$. Calculated % P 8.8

Allyl methacrylate. 5.2 g of diethylphosphorous acid and 5 g of allyl methacrylate gave 6.2 g of allyl β -diethylphosphonobutyrate (Table 3, compound 10).

Found % P 11.5; 11.4

$C_{11}H_{21}O_5P$. Calculated % P 11.7

SUMMARY

1. Dialkylphosphorous acids add on to methacrylamide, to give dialkylphosphonobutyramides.
2. The products of addition of higher dialkylphosphorous acids to methyl methacrylate, and of diethylphosphorous acid to alkyl methacrylates are described.

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A. E. Arbuzov Institute of Chemistry
Kazan Branch Academy of Sciences, U.S.S.R.

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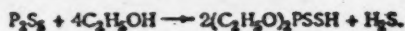
RESEARCHES IN THE FIELD OF PHOSPHORUS-ORGANIC COMPOUNDS

REACTION OF SULFIDES OF PHOSPHORUS WITH ALCOHOLS

M. I. Kabachnik and T. A. Mastryukova

The majority of methods for synthesis of phosphorus organic compounds, and in particular of esters and other derivatives of thio-acids of phosphorus, are based on the use of chloro-derivatives of phosphorus as starting products. This entails certain inconveniences, since halogen derivatives of phosphorus are sensitive to moisture, as a result of reaction with which from one to three (five) moles of hydrogen chloride or other halide are produced, and have to be removed from the sphere of reaction. Sulfides of phosphorus do not present these disadvantages, and are increasingly occupying the attention of chemists, as starting products for the synthesis of esters of thioacids of phosphorus. Up till now, however, the only sulfide used for this purpose has been P_4S_{10} (P_2S_5).

The reaction of phosphorus decaulfide with ethanol has been studied by Pishchinnika [1], who showed that the basic product is diethyl dithiophosphate:



Nothing is known of the behavior of the lower sulfides of phosphorus in this respect. We have studied the reactions with alcohols of the sulfides P_4S_6 , P_4S_8 , and P_4S_7 (and also the product of fusing together a 1:1 molecular mixture of phosphorus and sulfur), and we found that these sulfides can serve for the preparation not only of products of the type $(RO)_2PSSH$, as was shown by Pishchinnika for the sulfide P_4S_{10} but also for various other classes of phosphorus thio-acid derivatives, including those of tervalent phosphorus.

The heptasulfide P_4S_7 reacts with lower alcohols in the cold, and with higher ones when heated. The products are a mixture of liquid substances, and hydrogen sulfide is evolved, with an admixture of phosphine. Fractionation of the products obtained with ethanol, propanol, and n-butanol gives three distinct fractions, of which the highest b.p. one is the ester of dithiophosphoric acid of the composition $(RO)_2(RS)PS$. The middle fraction appears to belong to the known series of partial esters of dithiophosphoric acid of the structure $(RO)_2PSSH$, and the lowest b.p. fraction consists of partial ester of thiolphosphorous acid $(RO)_2PSH$.

The sulfide P_4S_7 reacts somewhat differently with methanol, giving only two products, trimethyl dithiophosphate $(CH_3O)_2(CH_3S)PS$ and dimethyl thiophosphite $(CH_3O)_2PSH$.

The formation of the three products $(RO)_2PSH$, $(RO)_2PSSH$, and $(RO)_2(RS)PS$, together with hydrogen sulfide and small amounts of phosphine and phosphorus, from the reaction between P_4S_7 and alcohols testifies to the complex nature of this reaction, and possibly to the existence of several parallel reactions proceeding simultaneously. We would here refer to the complex nature of the reaction of hydrolysis of the sulfide P_4S_7 [2].

TABLE 1

Formula	B.p., °C/p in mm	d_4^{20}	n_D^{20}	MR*		Yield** %
				Found	Calc.	
$(CH_3O)_2PSH$	52-53.5/16.5	1.1892	1.4768	29.93	29.78	5.8
$(C_2H_5O)_2PSH$	67.5-68.5/12	1.0828	1.4597	38.91	39.02	14.5
$(n-C_3H_7O)_2PSH$	62-63/3	1.0290	1.4581	48.27	48.26	19.0
$(iso-C_3H_7O)_2PSH$	49-50/3	1.0135	1.4541	48.64	48.26	21.8
$(n-C_4H_9O)_2PSH$	89-90/4	0.9974	1.4583	57.48	57.50	20.8

* The calculated MR is derived from the formula $\begin{matrix} S \\ \diagup \\ RO-P \\ \diagdown \\ H \end{matrix}$, taking the constants found by one of us [4] as for thioketones, the atomic refractivity of sulfur was taken as being 9.70.

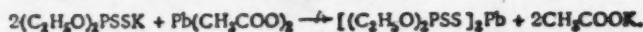
** Molar-percentage of phosphorus contained in P_4S_7 and converted into $(RO)_2PSH$.

The triesters of monothio-phosphorous acid have previously been described by Arbuzov and Nikanorov [3], while the diesters $(RO)_2PSH$ have not previously been prepared; their properties are given in Table 1, below.

The dialkyl thiophosphites

are colorless, mobile liquids with a characteristic odor. They are soluble in organic solvents and in aqueous alcohol, giving solutions neutral to litmus. They are insoluble in water, and are hydrolyzed by acids and alkalis, and readily oxidized by nitric acid. The tervalent phosphorus content was determined by alkaline hydrolysis followed by heating with hydrochloric acid, in order to eliminate hydrogen sulfide, and then by treatment with mercuric chloride. Dialkyl thiophosphites react with sodium, with evolution of hydrogen.

The structure of the second product of reaction of phosphorus heptasulfide with alcohols appears from the analytical data, the results of titration, and cryoscopic determination of molecular weight, to correspond with the formula $(RO)_2P(SH)_2$. Substances of this structure have been known for over 90 years, but all the workers who obtained them described them as undistillable syrups, only the salts being taken for analysis. It was natural to suppose that our esters, which could readily be distilled in vacuum, were isomeric with the known dialkyl thiophosphates; we found, however, that our esters $(RO)_2PSSH$ had identical chemical properties with the known esters of dithiophosphoric acid. The lead salt prepared from our diethyl dithiophosphate was found to be identical with the known lead salt $[(C_2H_5O)_2PSS]_2Pb$, prepared according to Martin and co-workers [6], by the reaction:



Both salts melted at 74.5–75.5°, mixed m.p. 75–76°. It is concluded that our dialkyl dithiophosphates have the formula $(RO)_2PSSH$; they were first prepared by us in a pure form. The constants of our esters are given in Table 2.

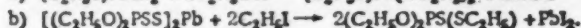
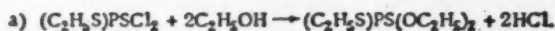
TABLE 2

Formula	B.p. °C/p in mm	d_4^{20}	n_D^{20}	MR*		Yield %
				Found	Calc.	
$(C_2H_5O)_2PSSH$	97-99/12	1.1650	1.5165	47.68	47.58	15.4
$(n-C_3H_7O)_2PSSH$	85-86/3	1.1040	1.4987	56.88	56.82	6.5
$(iso-C_3H_7O)_2PSSH$	70.5-71.5/3	1.0913	1.4920	56.89	56.82	25.4

* $AR_{S_2} = 9.70$; $AR_{S_4} = 9.34$

The dialkyl dithiophosphates are colorless, mobile, highly refractive liquids, with a smell of hydrogen sulfide. They are soluble in organic solvents and in aqueous alkalis. They can be titrated as strong acids in aqueous and alcoholic solution.

Triethyl dithiophosphate $(C_2H_5O)_2PS(SC_2H_5)$ has been synthesized by Pishchimuka [1] in two ways:



The highest b.p. fraction obtained by us from the reaction between P_4S_7 and ethanol has the same physical constants as does Pishchimuka's triethyl dithiophosphate, which we also prepared by reaction (b) above. Table 3, below, gives the physical constants of the ester $(C_2H_5O)_2PS(SC_2H_5)$, prepared in different ways.

TABLE 3

Method of preparation	Author	B.p. °C/p in mm	d	n_D^{20}
$P_4S_7 + C_2H_5OH$	This paper	115-115.5/10	d_4^{20} 1.1168 d_4^{20} 1.1383	1.5013
$P_4S_{10} + C_2H_5OH$ through the Pb salt + C_2H_5I	" "	116-117/12	d_4^{20} 1.1156	1.5034
Ditto	Pishchimuka	128/20	d_4^{20} 1.1340	-

prepared by us by the reaction between P_4S_7 and alcohols.

In order finally to show the identity of the esters obtained by both methods we prepared the double salt with mercuric iodide, of the composition $(C_2H_5O)_2PS(SC_2H_5)_2 \cdot 2HgI_2$. These salts all melted at 85–86°, alone or in mixtures.

Table 4 gives the descriptions of the trialkyl dithiophosphates

Two series of products were obtained from the reaction between phosphorus hexasulfide P_4S_6 * and methanol, ethanol, or propanol, viz., the dialkylthiophosphites $(RO)_2PSH$ and the trialkyl dithiophosphates $(RO)_2PS(SR)$; the acid esters $(RO)_2PSSH$ were not obtained at all. Phosphorus hexasulfide P_4S_6 also gives two products with isopropanol, these being $(iso-C_3H_7O)_2PSH$ and $(iso-C_3H_7O)_2PSSH$; triisopropyl dithiophosphate is not formed in this case. Phosphorus

* It cannot yet be taken as absolutely certain that the sulfide P_4S_6 exists. Glan [8] believes that an individual substance of this composition exists, but Mai [9] found that prolonged crystallization of a melt of the composition P_4S_2 gave the sulfide P_4S_7 . Pernert and Brown [10] believe, on the basis of published work, that the sulfide P_4S_6 is not an individual substance.

pentasulfide P_5S_5 gave two products with ethanol, viz $(C_2H_5O)_2PSH$ and $(C_2H_5O)_2PS(SC_2H_5)$, and the same products were given by a phosphorous-sulfur melt of the composition P_4S_4 , although the yields were much lower than with P_4S_7 or P_4S_8 .

TABLE 4

Formula	B.p. °C/p in mm	d_4^{20}	n_D^{20}	Parachor		MR*		Yield, %
				Found	Calc.	Found	Calc.	
$(CH_3O)_2PS(SCH_3)$	101-101.5/16.5	1.2415	1.5292	343.7	341.3	42.74	42.74	42.3
$(C_2H_5O)_2PS(SC_2H_5)$	115-115.5/10	1.1168	1.5013	460.4	457.8	56.65	56.60	11.0
$(i\text{-}C_3H_7O)_2PS(SC_3H_7)$	115-116/3	1.0561	1.4955	565.6	576	70.75	70.46	6.2
$(\text{iso-}C_3H_7O)_2PS(SC_3H_7)$	91-92/3	1.0351	1.4843	—	—	70.80	70.46	3.1
$(n\text{-}C_4H_9O)_2PS(SC_4H_9)$	148-149/4	1.0159	1.4859	—	—	84.20	84.32	9.6

* In calculation of MR we took for sulfur $AR_{S_2} = 9.70$ and $AR_S = 8.84$.

EXPERIMENTAL

Reaction of Alcohols with Sulfides of Phosphorus

The reactions were conducted in flasks fitted with reflux condensers and calcium chloride tubes. The lower alcohols began to react without heating, but the reaction was in all cases completed on a boiling water bath. The mixture was then filtered, excess of alcohol was distilled off from the filtrate, and the residue was fractionally distilled 3-4 times in a stream of carbon dioxide. The sulfides of phosphorus were prepared in the usual way, by melting together appropriate amounts of sulfur and red phosphorus, in an iron crucible [8].

Reaction of P_4S_7 with methanol. 52.2 g of sulfide P_4S_7 and 57.6 g of absolute methanol were allowed to react, and the product was 3 times fractionally distilled, at 16.5 mm., giving the fractions:

Fr. I. B.p. 53-53.5°/16.5 mm; 4.3 g; d_4^{20} 1.1892; n_D^{20} 1.4768

Found %: C 19.17; 19.24; H 5.43; 5.33; P 24.52; 24.42; MR 29.93

$C_2H_5O_2PS$. Calculated %: C 19.05; H 5.55; P 24.60; MR 29.78

Fr. II. B.p. 53.5-101°/16.5 mm; 3.7 g; a mixture.

Fr. III. B. p. 101-101.5°/16.5 mm; 43.0 g; d_4^{20} 1.2415; n_D^{20} 1.5292; σ_{20} 37.88 dynes/cm

Found %: C 21.07; 20.78; H 5.13; 5.38; P 17.90; 18.22; MR 42.74; P 343.7

$C_2H_5O_2PS_2$. Calculated %: C 20.93; H 5.22; P 18.04; MR 42.74; P 342.0

Reaction of P_4S_8 with methanol. 47.4 g of the sulfide P_4S_8 and 60.4 g of methanol gave the following fractions after two distillations at 8 mm:

Fr. I. B.p. 44-45°/8 mm; 5.1 g; n_D^{20} 1.4765; $(CH_3O)_2PSH$

Fr. II. B.p. 45-86°/8 mm; 2.1 g; a mixture

Fr. III. B.p. 86-87°/8 mm; 19.7 g; n_D^{20} 1.5272; $(CH_3O)_2PS(SCH_3)$

Reaction of P_4S_7 with ethanol. 58 g of sulfide P_4S_7 and 80 g of ethanol give, after four redistillations, the following fractions:

Fr. I. B.p. 67.5-68.5°/12 mm; 15.25 g; n_D^{20} 1.4597; d_4^{20} 1.0828 (compare experiment with P_4S_8); $(C_2H_5O)_2PSH$

Fr. II. B.p. 68.5-97°/12 mm; 2.0 g; a mixture

Fr. III. B.p. 97-98°/12 mm; 19.1 g; n_D^{20} 1.5105; d_4^{20} 1.1650; σ_{20} 31.70 dynes/cm

Found %: C 25.83; 25.97; H 6.10; 6.12; P 16.53; 16.69; MR 47.68; P 378.8; MB (Mol. Wt. cryoscopically, in benzene) 182.7.

$C_4H_{11}O_2PS_2$. Calculated %: C 25.84; H 5.91; P 16.67; MR 47.58; P 379.8; MB 186.

Fr. IV. B.p. 98-115°/12-10 mm; 5.73 g; a mixture

Fr. V. B.p. 115-115.5°/10 mm; 15.8 g; n_D^{20} 1.5013; d_4^{20} 1.1168 (compare with experiment with P_4S_8) - $(C_2H_5O)_2(C_2H_5S)PS$

Lead diethyl dithiophosphate was obtained from 1.86 g of diethyl dithiophosphate and 1.64 g of lead acetate in neutral aqueous solution. Recrystallization from ethanol gave 2.0 g of white, finely crystalline salt, m.p. 75-76°.

Found %: C 16.68; 16.59; H 3.75; 3.50
 $C_6H_{12}O_4P_2S_4Pb$. Calculated %: C 16.63 H 3.46

The same salt was prepared by the method of Mastin et al [6]: 6.6 g of diethyl thiophosphoryl chloride ($C_2H_5O_2PSCl$), prepared according to Fletcher et al. [7] (b.p. 90.5-91.5°/19 mm.; n_D^{20} 1.4705; d_4^{20} 1.1899) was added drop by drop to an alkaline solution of potassium hydrosulfide (from 3.5 g of KOH), the mixture was heated on a water bath for 2 hours, the solution was filtered, and the filtrate was evaporated down. The residue was treated with lead acetate, and the lead salt so obtained was recrystallized, giving 1.8 g of colorless, finely crystalline salt, m.p. 74.5-75.5°; published values for m.p. 74° [6], 74° [7], mixtures gave no depression of m.p.

Ethylation of lead diethyl dithiophosphate (by Pishchimuka's method). 10 g of the lead salt of the diethyl ester obtained from an experiment with P_4S_3 was heated with 5.6 g of ethyl iodide for 90 minutes on a water bath, the solution was filtered off from the lead iodide which forms, and the filtrate was fractionally distilled, giving 6.1 g (82.3% yield) of triethyl dithiophosphate, b.p. 116-117°/12 mm; n_D^{20} 1.5034; d_4^{20} 1.1156.

Double Salt of Mercuric Iodide and Triethyl Dithiophosphate ($C_2H_5O_2PS(SC_2H_5)_2 \cdot 2HgI_2$)

a) From the ester obtained from P_4S_3 . 10.7 g of triethyl dithiophosphate was heated in an oil bath at 95-110° with 45.4 g of mercuric iodide, for 80 min., and the product was recrystallized from alcohol, giving 39.0 g of double salt, m.p. 79-82°, rising to 85-86° after a second recrystallization.

b) From the ester obtained from ethylation of lead diethyl dithiophosphate. The m.p. was 85-86°, mixed m.p. with above product, 85-86°; Pishchimuka gives an m.p. of 86°.

Reaction of P_4S_3 with ethanol. 50.8 g of the sulfide P_4S_3 and 69 g of absolute ethanol were allowed to react, and the product was distilled three times, giving the fractions:

Fr. I. B.p. 63-65.5°/11 mm; 2.5 g

Fr. II. B.p. 65.5-66.5°/11 mm; 26.3 g; n_D^{20} 1.4592; d_4^{20} 1.0825.

Found %: C 31.35; 31.18; H 7.13; 7.30; S 20.55; 20.45; P 20.35; 20.35; MR 38.91
 $C_4H_{10}O_2PS$. Calculated %: C 31.17; H 7.07; S 20.78 P 20.13; MR 39.02

Fr. III. B.p. 66.5-110°/9-11 mm; 2.5 g; a mixture

Fr. IV. B.p. 110-111°/9 mm; 20.1 g; n_D^{20} 1.5015; d_4^{20} 1.1165; d_4^{25} 1.1383; σ_{25} 33.09 dynes/cm.

Found %: C 33.78; 34.00; H 7.17; 7.30; S 29.85; 30.09; P 14.69; 14.37; MR 56.65; P 460.4;
M (cryoscopic, in benzene) 209.9

$C_6H_{12}O_2PS_2$. Calculated %: C 33.64; H 7.01; S 29.95; P 14.49; M 56.60; P 459.0; M 214.

Determination of trivalent phosphorus in Fraction II. ($C_2H_5O_2PSH$). A weighed amount of diethyl thiophosphite was dissolved in 20 ml of 0.1N-NaOH, and the solution was heated in a Kjeldahl flask for 10 hours, passing a stream of CO_2 . It was then made acid with 0.1N HCl, and boiled in a stream of CO_2 until the emerging gas no longer contained hydrogen sulfide, after which phosphorous acid was oxidized with mercuric chloride, in the usual way. The calomel formed was collected, washed and dried at 105°.

Found %: P 20.25; 20.17

$C_4H_{10}O_2PS$. Calculated %: P 20.13

Reaction of P_4S_3 with ethanol. 28.4 g of the sulfide P_4S_3 was heated for 10 hours with 46.0 g of absolute ethanol, the solution was filtered from the solid residue, which weighed 7.4 g, and the filtrate was fractionated (3 distillations) at 9.5 mm, giving the fractions:

Fr. I. B.p. 59.5-61°/9.5 mm; 0.9 g

Fr. II. B.p. 61-61.5°/9.5 mm; 8.3 g; n_D^{20} 1.4589; d_4^{20} 1.0805.

Found MR 38.96; Calculated MR 39.02 ($C_2H_5O_2PSH$)

Fr. III. 61.5-105°/9.5 mm; 3.4 g; a mixture

Fr. IV. 105-105.5°/9.5 mm; 9.3 g; n_D^{20} 1.5020; d_4^{20} 1.1157.

Found MR 56.60; Calculated MR 56.60 ($C_6H_5O_2PS(SC_2H_5)$)

Reaction of 1:1 atomic sulfur-phosphorus melt with ethanol. 49.8 g of the melt was treated with 80 g of ethanol, and the solution was filtered after completion of the reaction (solid residue 17.3 g). The filtrate gave the following fractions after two distillations at 11 mm:

Fr. I B.p. 64-65.5°, 1.3 g

Fr. II B.p. 65.5-68.5, 16.3 g; n_D^{20} 1.4592 ($C_6H_5O_2PSH$)

Fr. III B.p. 68.5-112°, 7.0 g

Fr. IV B.p. 112-112.5°, 19.3 g; n_D^{20} 1.5031 ($C_6H_5O_2PS(SC_2H_5)$)

Reaction of P_4S_7 with propanol. 52.2 g of the sulfide P_4S_7 and 120 g of absolute n-propanol were taken. The product gave the following fractions after 4 distillations at 3 mm:

Fr. I B.p. 59-62°, 0.5 g.

Fr. II B.p. 62-63°, 20.8 g; n_D^{20} 1.4581; d_4^{20} 1.0290.

Found % P 17.12; 17.20; MR 48.27

$C_6H_{13}O_2PS$. Calculated % P 17.03; MR 48.28

Fr. III B.p. 63-85°, 4.6 g; a mixture

Fr. IV B.p. 85-86°, 8.3 g; n_D^{20} 1.4987; d_4^{20} 1.1040.

Found % P 14.37; 14.45; MR 56.88

$C_6H_{13}O_2PS_2$. Calculated % P 14.49; MR 56.82

Fr. V B.p. 86-115°, 3.7 g; a mixture

Fr. VI B.p. 115-116°, 11.0 g; n_D^{20} 1.4955; d_4^{20} 1.0561; σ_{20} 29.91 dynes/cm

Found % P 12.02; 12.21; MR 70.75; P 565.6

$C_6H_{21}O_2PS_2$. Calculated % P 12.11; MR 70.46; P 576.0

Reaction of P_4S_8 with n-propanol. 47.4 g of the sulfide P_4S_8 and 108 g of n-propanol give a product, which after three vacuum distillations at 4 mm gave the fractions:

Fr. I B.p. 74.5-75.5°, 30.2 g; n_D^{20} 1.4581; d_4^{20} 1.0290

Found MR 48.27

$C_6H_{13}O_2PS$. Calculated MR 48.26

Fr. II B.p. 75.5-123°, 6.0 g; a mixture

Fr. III B.p. 123-124°, 9.7 g; n_D^{20} 1.4952; d_4^{20} 1.0561

Found MR 70.71

$C_6H_{21}O_2PS_2$. Calculated MR 70.46

Reaction of P_4S_7 with isopropanol. 52.2 g of the sulfide P_4S_7 and 120 g of isopropanol give a product, from which the following fractions were obtained, at 3 mm:

Fr. I B.p. 48-49°, 0.5 g

Fr. II B.p. 49-50°, 23.8 g; n_D^{20} 1.4541; d_4^{20} 1.0135.

Found % P 17.10; 17.13; S 17.55; 17.55; MR 48.64

$C_6H_{13}O_2PS$. Calculated % P 17.03 S 17.53; MR 48.26

Fr. III B.p. 50-70.50; 3.8 g; a mixture

Fr. IV B.p. 70.5-71.5°, 32.6 g; n_D^{20} 1.4920; d_4^{20} 1.0913

Found % P 14.40; 14.46; S 29.62; 29.35; MR 56.89

$C_6H_{13}O_2PS_2$. Calculated % P 14.49; S 29.91; MR 56.82

Fr. V B.p. 71.5-91°, 3.7 g; a mixture

Fr. VI B.p. 91-92°, 4.7 g; n_D^{20} 1.4843; d_4^{20} 1.0351

Found % S 24.05; 25.17

$C_6H_{21}O_2PS_2$. Calculated % S 25.00

Reaction of P_2S_5 with isopropanol. 47.4 g of the sulfide P_2S_5 and 108 g of isopropanol gave a product, from which the following fractions were obtained after three distillations:

Fr. I B.p. 47-48°/3 mm; 26.0 g; n_D^{20} 1.4533; d_4^{20} 1.0132 ($iso-C_3H_7O_2$)₂PSH

Fr. II B.p. 48-56°/3-7 mm; 5.5 g; a mixture

Fr. III B.p. 56-97°/7 mm; 4.0 g; n_D^{20} 1.4936; d_4^{20} 1.0921 ($iso-C_3H_7O_2$)₂PSSH

Reaction of P_2S_7 with n-butanol. 52.2 g of the sulfide P_2S_7 and 133.2 g of n-butanol were allowed to react, and the product was distilled at 4 mm., giving the fractions:

Fr. I B.p. 101-105°, 29.0 g

Fr. II B.p. 105-110°, 20.5 (with decomposition)

Decomposition then became increasingly more intense, so that distillation was stopped, leaving 57 g of a bright yellow syrup in the flask; this residue was treated separately. The distillates were redistilled three times at 4 mm, giving

Fr. I B.p. 89-90°, 26.2 g; n_D^{20} 1.4583; d_4^{20} 0.9974

Found %: P 14.62; 14.53; MR 57.48

$C_4H_9O_2PS$. Calculated %: P 14.76; MR 57.50

Fr. II B.p. 90-148°, 4.3 g; a mixture

Fr. III B.p. 148-149°, 13.4 g; n_D^{20} 1.4859; d_4^{20} 1.0159

Found %: P 10.52; 10.50; MR 84.20

$C_{12}H_{27}O_2PS_2$. Calculated %: P 10.40 MR 84.32

The undistilled residue was treated with a small excess of 0.1 N NaOH, and the aqueous layer was separated from the oil, and extracted with ether. The ethereal extract was added to the oil, and the solution was dried with calcium chloride; it yielded a further 3.6 g of tributyl dithiophosphate, b.p. 148-149°/4 mm; n_D^{20} 1.4863.

The aqueous layer was evaporated down on the water bath, and excess of aqueous mercuric chloride was added. The precipitate was thrice recrystallized from alcohol, giving 4.9 g of mercury dibutyl dithiophosphate, m.p. 60-61°. The same salt was prepared by the method of Mastin et al [7], also m.p. 60-61°, mixed m.p. with our salt 60-60.5°.

SUMMARY

1. A study has been made of the reactions of the sulfides of phosphorous P_2S_7 , P_2S_6 and P_2S_5 with alcohols.
2. Three types of products are obtained from P_2S_7 and ethanol, propanol or butanol, viz., $(RO)_2PSH$, $(RO)_2PSSH$, and $(RO)_2(RS)PS$.
3. The sulfide P_2S_7 and methanol give the esters $(CH_3O)_2PSH$ and $(CH_3O)_2(CH_2S)PS$.
4. The sulfide P_2S_6 reacts with alcohols to give esters of the types $(RO)_2PSH$ and $(RO)_2(RS)PS$. Only with isopropanol does this sulfide give the esters $(iso-C_3H_7O)_2PSH$ and $(iso-C_3H_7O)_2PSSH$.
5. The same products are obtained from the sulfide P_2S_5 , or the 1:1 atomic sulfur-phosphorus melt, and alcohols as with the sulfide P_2S_6 , but the yields are lower.
6. The dialkyl dithiophosphates $(RO)_2PSSH$ have for the first time been prepared pure; they are liquids, which can be distilled in vacuum.

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Institute of Organic Chemistry
Academy of Sciences U.S.S.R.

STUDIES IN THE FIELD OF CYANINE DYES

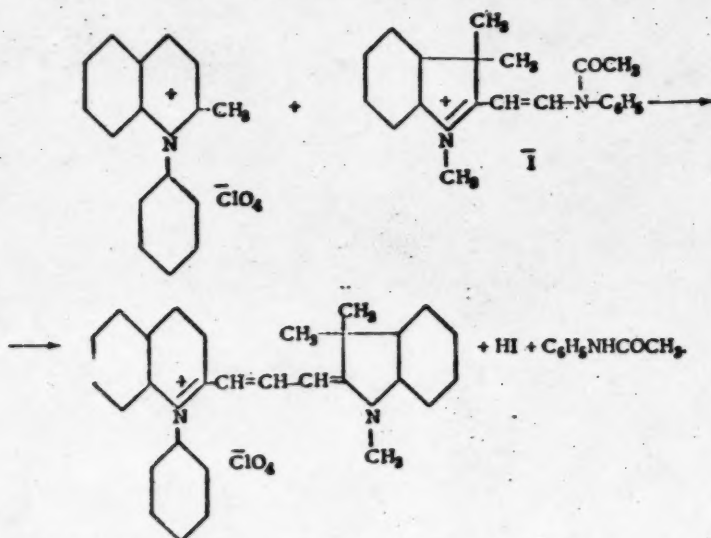
PART 3. ASYMMETRICAL CARBOCYANINES FROM N-ARYLQUINALDINE AND INDOLENINE

G. T. Pilyugin

The asymmetrical cyanines have only relatively recently been studied, owing chiefly to the much greater difficulty of preparing them, as compared with the symmetrical cyanines, which are of particular importance as sensitizers of silver bromide in photographic emulsions. The asymmetrical cyanines are thus of considerable interest, from both the theoretical and the practical points of view.

Asymmetrical cyanines containing an N-arylquinoline ring were first described by the author [1]. It is of interest, in studying the structure of this class of dyes, to investigate the effect on the color of the dye of varying the heterocyclic component and the substituent in various positions of the molecule.

We shall in the present paper consider asymmetrical cyanines formed from N-arylquinolinium salts and the intermediate product 2-B-anilinoethyl-3,3-dimethylindolenine methiodide [2]:



The N-arylquinoindocyanines obtained are shown in the Table, which also gives, for the sake of comparison, the absorption maxima of the corresponding symmetrical dyes.


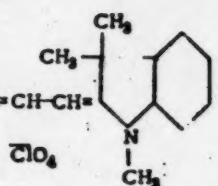

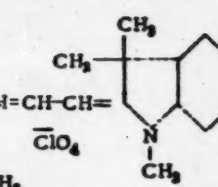
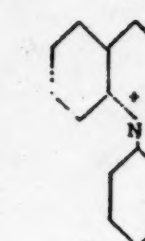
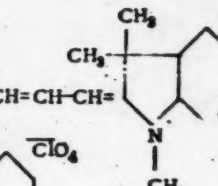
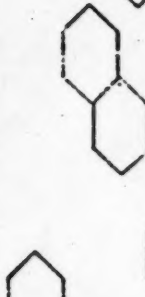
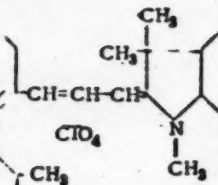
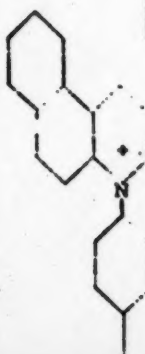
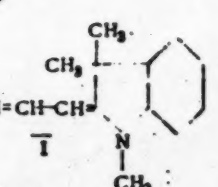
The presence of N-aryl groups in the quinoline ring gives insignificant bathochromic shifting of the absorption maximum of the asymmetrical dyes, as compared with alkyl substituents. This led to the much smaller hypsochromic shift of the absorption maximum of the asymmetrical dye from the additive value of the maximum for the corresponding symmetrical dyes. Thus, for example, the dye obtained from the quaternary salt of quinaldine ethiodide and the intermediate product of indolenine has an absorption maximum at 559.5 mμ, and the hypsochromic shift of the maximum from the additive value amounts here to 15.0 mμ, whereas the analogous dye with a phenyl substituent has an absorption maximum at 572 mμ, and the hypsochromic shift from the additive value is here 7.5 mμ.

In comparing the dyes obtained with each other, taking as the basis for comparison the dye with a N-phenyl group (No. 1), we observe the following mutual effects of various structural groupings. Introduction of the methyl group into position 6 leads to a bathochromic shift of maximum absorption of 6 mμ (No. 2), whereas a 6-methyl

TABLE

No.	Formula of dye		Absorption maximum, mμ				Deviation from addition rule	
	(I)	(II)	Symmetrical from (I)	Symmetrical from (II)	Asymmetrical from (I+II) 2	Asymmetrical (found)	Hypochromic	Bathochromic
1			614	545	579.5	572	7.5	-
2			620	545	582.5	578	4.5	-
3			622	545	583.5	572	11.5	-
4			625	545	585	580	5	-

TABLE (Continued)

Serial No.	Formula of dye		Absorption maximum, mμ				Deviation from addition rule	
			Symmetrical from (I)	Symmetrical from (II)	Asymmetrical from (I+II)/2	Asymmetrical (found)		
	(I)	(II)					Hypsochromic	Bathochromic
5			645	545	595	580	15	-
6			642	545	543.5	585	8.5	-
7			618	545	581.5	574	7.5	-
8			644	545	594.5	580	14.5	-
9			654	545	599.5	585	14.5	-

group in the N-p-tolyl derivative has no effect on shift of the maximum (No. 3). A bathochromic shift of the absorption maximum of 8 m μ is found in the 6-methyl-N-naphthyl derivative (No. 4) and in the 5,6-benzo-N-phenyl derivative (No. 5), while the shift for the 7,8-benzo-N-o-tolyl derivative (No. 6) amounts to 13 m μ . Simultaneous presence of phenylene groups in the 5,6 position of the quinoline ring and in the N-aryl substituent (No. 9) gives a shift of 13 m μ . It is of interest that presence of a phenylene group in the N-aryl substituent has only a very small effect (No. 7); a similar finding has been reported for dyes of a symmetrical structure [7].

EXPERIMENTAL

(1-Phenylquinoline-2)-(1,3,3-trimethylindolenine-2)-trimethinecyanine perchlorate. 0.4 g of indolenine intermediate product (1 mol) and 0.34 g of phenylquinaldine perchlorate (1 mol. + 20% excess) were heated with 2 ml of pyridine for 30 min., keeping the mixture boiling gently. The dye was precipitated from the pyridine solution by adding a small amount of alcohol, collected, and washed with water, alcohol, and ether. The dye was recrystallized from alcohol, as platelets with a green metallic sheen, m.p. 180° (decomposition), yield 43%. Absorption maximum in ethanol solution 572 m μ .

Found % Cl 6.94
 $C_{29}H_{27}N_3O_4Cl$. Calculated % Cl 7.05

(1-Phenyl-6-methylquinoline-2)-(1,3,3-trimethylindolenine-2)-trimethinecyanine perchlorate. 0.2 g of the quaternary salt 1-phenyl-6-methylquinaldine perchlorate in 2 ml of pyridine and 0.18 g of indolenine derivative were heated at the b.p. for 30 min. with a few drops of acetic anhydride. The dye was precipitated from the cooled solution by addition of ether, and was collected, washed with alcohol and ether, and recrystallized, giving 0.12 g (44% yield) of dark red crystals, m.p. 215°, absorption maximum at 578 m μ .

Found % Cl 6.61
 $C_{30}H_{29}N_3O_4Cl$. Calculated % Cl 6.87

(1-p-Tolyl-6-methylquinoline-2)-(1,3,3-trimethylindolenine-2)-trimethinecyanine perchlorate. 0.25 g of quaternary salt (1.2 mol), 0.25 g of indolenine intermediate (1 mol) and 2 ml of pyridine were boiled under reflux for 30 min. with shaking. The dye was precipitated from the cooled solution by adding ether, and the precipitate was dissolved in alcohol. An equal volume of saturated aqueous potassium perchlorate was added to the solution, and the crystalline product was recrystallized from aqueous alcohol, giving light green crystals of m.p. 215-218° (decomposition), yield 27%, absorption maximum at 572 m μ .

Found % Cl 6.32
 $C_{31}H_{31}N_3O_4Cl$. Calculated % Cl 6.69

(1- α -Naphthyl-6-methylquinoline-2)-(1,3,3-trimethylindolenine-2)-trimethinecyanine perchlorate. A mixture of 0.3 g of 1- α -naphthyl-6-methylquinaldine iodide, 0.26 g of indolenine intermediate, and 2 ml of pyridine is boiled for 1 hr., adding a few drops of acetic anhydride during the process. The reaction product was treated with ether, and the residue was dissolved in ethanol (2 ml). Saturated aqueous potassium perchlorate was added, the mixture was heated to boiling, and left for 24 hrs. giving 0.13 g (43% yield) of violet crystals, with a metallic sheen, m.p. 252° (decomposition), absorption maximum 580 m μ . Alcoholic solutions of the dye were colored violet.

Found % Cl 6.41
 $C_{34}H_{31}N_3O_4Cl$. Calculated % Cl 6.26

(1-Phenyl-5,6-benzoquinoline-2)-(1,3,3-trimethylindolenine-2)-trimethinecyanine perchlorate. A mixture of 0.3 g of 2-B-acetanilidovinyl-1,3,3-trimethylindolenine iodide, 0.22 g of the quaternary salt of benzoquinoline perchlorate, and 2 ml of pyridine, with a few drops of acetic anhydride, were boiled, with constant shaking, for 40 min. The dye was precipitated from the solution by adding ether, and the precipitate was dissolved in 2 ml of alcohol, 2 ml of saturated aqueous potassium perchlorate were added, and the product was recrystallized from aqueous alcohol, giving a crystalline product with a metallic sheen, m.p. 239° (decomposition), yield 29%, absorption maximum at 580 m μ .

Found %: Cl 6.16
 $C_{33}H_{29}N_3O_4Cl$. Calculated % Cl 6.42

(1-o-Tolyl-7,8-benzoquinoline-2)-(1,3,3-trimethylindolenine-2)-trimethinecyanine perchlorate. A mixture of 0.15 g of 2-B-acetanilidovinyltrimethylindolenine iodide, 0.25 g of 1-o-tolyl-7,8-benzoquinoline perchlorate, 3 ml of pyridine, and a few drops of acetic anhydride was boiled for about 1 hr., cooled, ether was added, the

precipitate was collected, washed with water, alcohol, and ether, and recrystallized from aqueous alcohol, giving a product, m.p. 225° (decomposition), absorption maximum at 585 mμ. The alcoholic solution was colored lilac.

Found %: Cl 6.14
 $C_{34}H_{31}N_2O_4Cl$. Calculated %: Cl 6.28

(1- α -Naphthylquinoline-2)-(1,3,3-trimethylindolenine-2)-trimethinecyanine perchlorate. A mixture of 0.2 g of the quaternary salt α -naphthylquinaldine perchlorate, 0.16 g of 2- β -acetanilidovinyltrimethylindolenine methiodide, 2 ml of pyridine, and a few drops of acetic anhydride was boiled for 45 min., 5 ml of ether was added to the cooled solution, the precipitate was dissolved in 2 ml of ethanol, 2 ml of saturated aqueous potassium perchlorate and 5 ml of water were added to the warm solution, which was then boiled for 5 min. The finely crystalline product was collected, washed with ether, and recrystallized from aqueous alcohol, giving 0.1 g of dark blue crystals, m.p. 260° (decomposition), yield 30%, absorption maximum at 574 mμ. The alcoholic solution of the dye was colored bluish red.

Found %: Cl 6.27
 $C_{33}H_{29}N_2O_4Cl$. Calculated %: Cl 6.42

(1-o-Tolyl-5,6-benzoquinoline-2)-(1,3,3-trimethylindolenine-2)-trimethinecyanine perchlorate. A mixture of 0.2 g of indolenine intermediate, 0.22 g of the quaternary salt tolylbenzoquinaldine iodide, 2 ml of pyridine, and a few drops of acetic anhydride was boiled for 50 min, 5 ml of ether was added to the cooled solution, the precipitate was collected, dissolved in alcohol, and reprecipitated with ether. 2 ml of saturated aqueous potassium perchlorate was added to a boiling alcoholic solution of the dye, and the salt was collected the next day, washed with alcohol and ether, and recrystallized from aqueous alcohol, giving 0.065 g (26.8% yield) of dark violet crystals with a metallic sheen, m.p. 225° (decomposition), absorption maximum 580 mμ.

Found %: Cl 6.08
 $C_{34}H_{31}N_2O_4Cl$. Calculated %: Cl 6.28

(1- β -Naphthyl-5,6-benzoquinoline-2)-(1,3,3-trimethylindolenine-2)-trimethinecyanine iodide. A mixture of 0.4 g of indolenine intermediate (1 mol), 0.48 g of the quaternary salt naphthylbenzoquinaldine iodide (1 mol + 20% excess), 2 ml of pyridine, and 0.5 ml of acetic anhydride was boiled for 40 min. The color of the solution rapidly changed from reddish violet to blue. The dye was precipitated by the addition of ether to the cooled solution, and was recrystallized from aqueous alcohol; the yield of crude product was 0.21 g, or 37.5% which fell to 22% after recrystallization. Dark blue crystals, m.p. 248-250°, absorption maximum at 585 mμ.

Found %: I 20.38
 $C_{37}H_{31}N_2I$. Calculated %: I 20.15

SUMMARY

1. New carbocyanine dyes with an asymmetrical structure have been prepared by the reaction of quaternary salts of N-arylquinaldine with indolenine intermediate product.
2. The properties of the new asymmetrical dyes have been studied.

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Institute of Organic Chemistry
Academy of Sciences USSR
Chernovits: State University

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- See Consultants Bureau English Translation, p. 347.
- See Consultants Bureau English Translation, p. 491, 492.

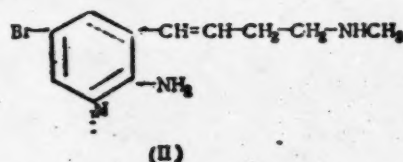
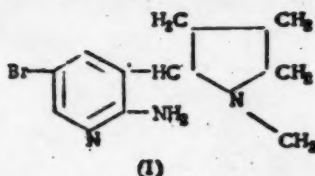
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ULTRA-VIOLET ABSORPTION SPECTRA OF SOME DERIVATIVES OF PYRIDINE AND NICOTINE

PART 3 [I]

K. A. Zhukova, M. S. Kondakova, and Ya. L. Goldfarb

Goldfarb and Kondakova [2], acting on 5-bromo-2-aminonicotine (I) with acetic anhydride, obtained an isomer to which they assigned the structure (II), on the grounds that under similar conditions 2-amino-nicotine gives 2-aminometaninicotine:



It was supposed that the action of acetic anhydride consists in the opening of the pyrrolidine ring of molecule (I), giving a new molecule with a double bond in the side-chain conjugated with those of the pyridine ring. This sort of change in the degree of unsaturation of the molecule involves, in particular, a bathochromic shift in the absorption spectrum [3]; for this reason the presence of such a shift, in comparing the absorption curves of 5-bromo-2-aminonicotine and of the new base derived from it, could be taken as confirmatory evidence that the latter is 5-bromo-2-aminometaninicotine. For this reason we have undertaken the study of the ultra-violet absorption spectra of this compound, and of others of related structure. The same method of comparing spectra was later found useful in solving certain problems arising from a study of the transformations of 5-bromo-2-aminometaninicotine (II). The results obtained are given in Table 1*, and the absorption curves serving as bases for comparison are shown in Figs. 1 and 2.

The first maximum of the absorption band of 2-aminometaninicotine, the structure of which as a compound with a double bond in the side-chain conjugated with those of the pyridine ring has been established by chemical methods [4], is shifted in the long-wave part of the spectrum by about 25 mμ, as compared with the corresponding maximum of 2-aminonicotine. The absorption curve of 2-amino-3-(4'-dimethylamino-but-1'-enyl)-pyridine, which may be regarded as a methylation product of 2-aminometaninicotine, scarcely differs with respect to the position and magnitude of the absorption maximum (Table 1) from that for the latter compound. Such a coincidence of the absorption spectra was to be expected, since the introduction of a methyl group, which itself does not perceptibly affect the absorption spectrum, does not in the given case involve any rearrangement of the double bonds.

Hydrogenation of 2-aminometaninicotine gives 2-amino-3-(4'-methylaminobutyl)-pyridine, in which both bands (Fig. 1) are shifted in the direction of shorter wave-lengths, and the absorption curve becomes practically identical with those of 2-aminopyridine or 2-aminonicotine.

Systems of a higher degree of unsaturation than 2-aminometaninicotine are represented by 2-amino-3-buta-1',3'-dienylpyridine (Fig. 3), for which the maxima of the absorption bands are at 344 mμ (log E 4.11) and 270 mμ (log E 4.16), and are hence shifted considerably towards the red end of the spectrum, in comparison with the corresponding maxima for 2-aminometaninicotine. Hydrogenation of the unsaturated side-chain again gave, as could be expected, a system (2-amino-3-butyl-pyridine) spectrally indistinguishable from 2-aminopyridine or 2-aminonicotine.

It is evident from the data cited that the changes in the absorption spectra of substituted 2-aminopyridines are of the same nature as in other systems, arranged in order of increasing number of conjugated double bonds, i.e., formation of a new conjugated double bond involves a considerable shift of the absorption bands in the direction of

* The spectra are in all cases those obtained in ethanol solutions of the bases.

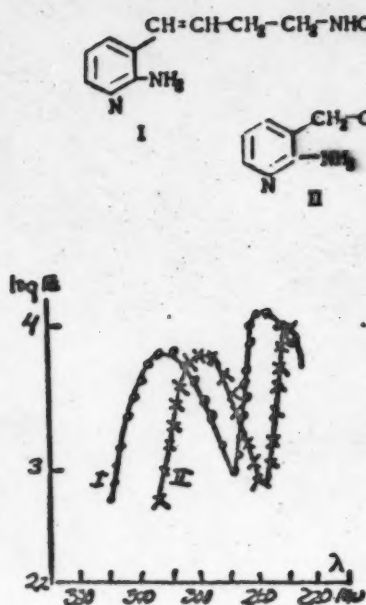


Fig. 1

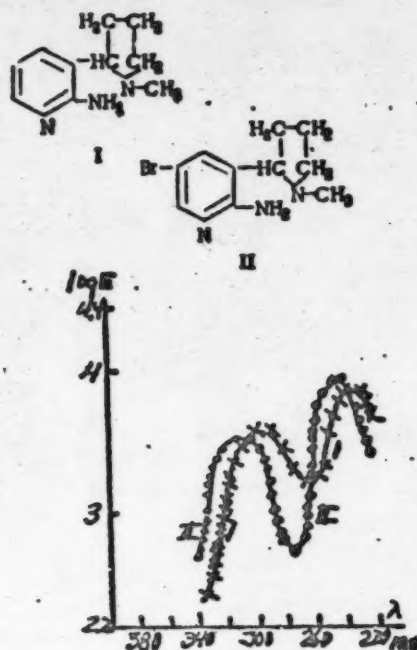


Fig. 2

longer wave lengths. A shift in the same direction, and of the same magnitude, is observed when we compare the spectra of 5-bromo-2-aminonicotine and of the base formed from it by the action of acetic anhydride (Fig. 4); this confirms our previously expressed view (*loc. cit.*) that this is 5-bromo-2-aminometaninicine, the first maximum of the absorption curve of which is at 335 mμ (log E 3.71). It thus appears that substitution of bromine in position 5 of the pyridine ring of 2-aminometaninicine leads to a further shift towards the red end of the spectrum, on the average of about 12 mμ.

The absorption curves of 5-bromo-2-aminometaninicine and of the product of its ring closure, in which the partly hydrogenated ring retains a double bond conjugated with the double bond system of the second ring, viz., 6-bromo-2-methylaminomethyl-1,2-dihydro-1,8-naphthiridine, differ only in the position of the second maximum, but are identical in all other respects (Fig. 5). In view of this, the data for the absorption spectrum of 6-bromo-2-methyl-1,8-naphthiridine are the more noteworthy.

The absorption curve for this compound has a first maximum shifted towards the ultra-violet, as compared with the former dihydronaphthiridine (Fig. 6), with a second maximum ending abruptly at 245 mμ; these two systems have radically different spectra. This effect appears to be a consequence of dehydrogenation of dihydronaphthiridine, which leads to production of a radically new chromophore (1,8-naphthiridine), with a new system of double bonds.

While studying the transformation of 5-bromo-2-aminometaninicine we found ourselves obliged to choose between structures A and B for the base of m. p. 127-129°, formed together with 6-bromo-2-methylamino-methyl-1,2-dihydro-1,8-naphthiridine by the action of alkali on 5-bromo-2-amino-3-(3'-bromo-4'-methylaminobut-1'-enyl)-pyridine:

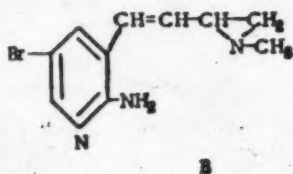
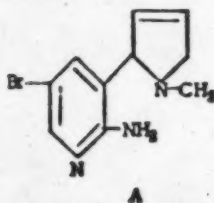
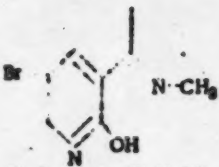


TABLE 1

Substance	Formula	1st max.	log E	2nd max.	log E
2-Aminonicotine		298	3.56	235	3.85
2-Amino-3-(4'-methylaminobut-1'-enyl)-pyridine (2-aminometan- cotine)		323	3.79	257	4.06
2-Amino-3-(4'-dimethylaminobut-1'-enyl)-pyridine		320	3.72	255	3.99
2-Amino-3-(4'-methylaminobutyl)- pyridine (2-aminodihydrometani- cotine)		298	3.78	240	3.96
2-Amino-3-buta-1',3'-dienyl pyridine		344	4.11	270	4.16
2-Amino-3-butylpyridine		295	3.62	238	3.8
5-Bromo-2-aminonicotine		310	3.52	245	3.92
5-Bromo-2-amino-3-(4'-methyl- aminobut-1'-enyl)-pyridine (5- bromo-2-aminometan- cotine)		335	3.71	255	3.92
6-Bromo-2-methylaminomethyl- 1,2-dihydro-1,8-naphthiridine		336	3.66	238	3.98
6-Bromo-2-methyl-1,8-naph- thiridine					
5-Bromo-2-amino-3-(1'-methyl- 2'-pyrrolinyl)-pyridine		315	3.82	247	4.2

TABLE 1 (Continued)

Substance	Formula	1st max.	log E	2nd max.	log E
5-Bromo-2-hydroxy-3-(1'-methyl-2'-pyrrolyl)-pyridine		318	3.66	238	3.98

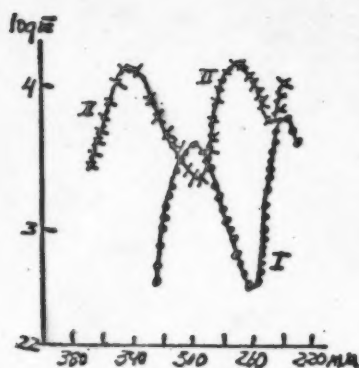
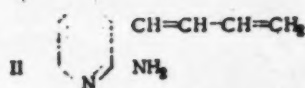
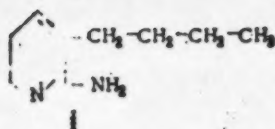


Fig. 3

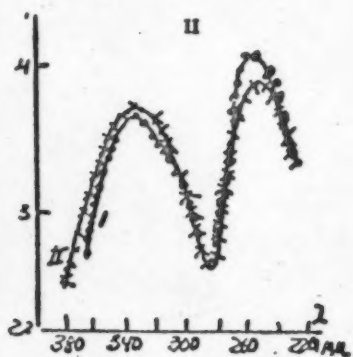
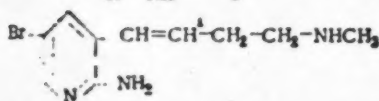
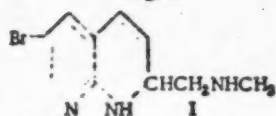


Fig. 5

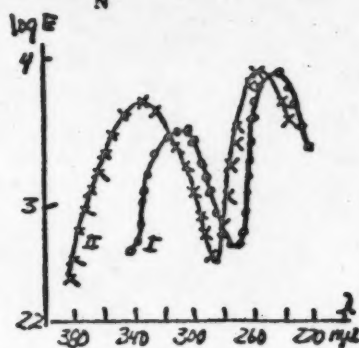
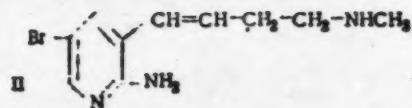


Fig. 4

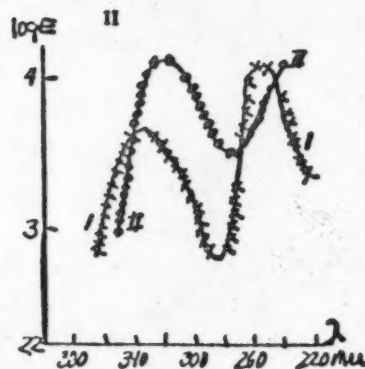
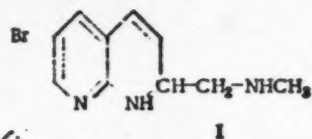


Fig. 6

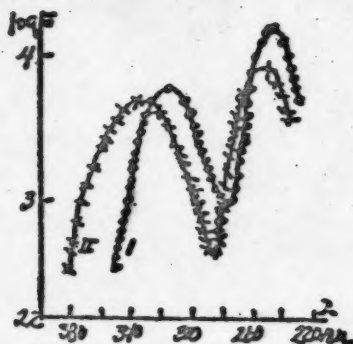
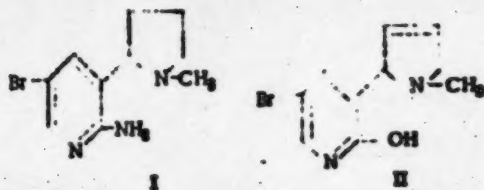
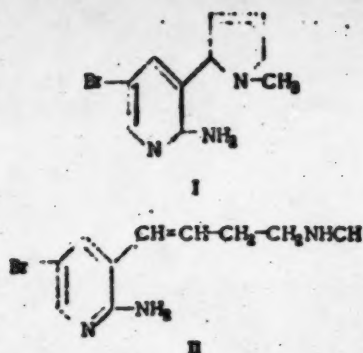


Fig. 7

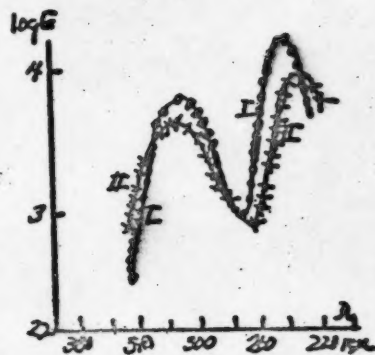


Fig. 8

A comparison of the absorption spectra of this base and of 5-bromo-2-aminonicotine enabled us to make the necessary choice (Fig. 7).

The spectra of bases of type B should not differ significantly from that of 5-bromo-2-aminonicotine, since the position of the double bond of the side-chain is the same, and the ethylenimino-ring does not cause any shift in the position of absorption bands due to presence of double bonds in the molecule [5]. If, therefore, the base of m.p. 127-129° had structure B, its absorption curve should in its general contours conform with that of 5-bromo-2-aminonicotine. This is not, however, found to be the case; the maxima of the absorption bands for the base of m.p. 127-129° are at 315 mμ (log E 3.82) and 247 mμ (log E 4.2), and for 5-bromo-2-aminonicotine are at 335 mμ (log E 3.71) and 255 mμ (log E 3.92). A very similar absorption curve is found for the product of reaction of nitrous acid on the base of m.p. 127-129°, 5-bromo-2-hydroxy-3-(1'-methyl-2'-pyrrolidinyl)-pyridine (Fig. 8).

The similarity of the absorption curves of the base and of 5-bromo-2-aminonicotine should also be noted, as being in agreement with our views on the structure of the base of m.p. 127-129°, as a derivative of dihydronicotine of structure A, in which the double bond is not conjugated with those of the pyridine ring.

EXPERIMENTAL

1. 2-Aminonicotine was prepared by the method of Chichibabin and Kirsanov [6], and was purified by vacuum distillation followed by recrystallization from ethanol-acetone mixture; it melted at 124-124.5°.

2. 2-Amino-3-(4'-methylaminobut-1'-enyl)-pyridine (2-aminometanicoline) was prepared by the method of Goldfarb and Karaulova [7], m.p. 81-82° after vacuum distillation and recrystallization from heptane.

3. 2-Amino-3-(4'-methylaminobutyl)-pyridine (2-aminodihydrometanicoline) was obtained by hydrogenation of 2-aminometanicoline in presence of platinum catalyst. It was purified as the perchlorate, after regeneration from which it was recrystallized from heptane; m.p. 84-85°.

4. 2-Amino-3-(4'-dimethylaminobut-1'-enyl)-pyridine was prepared by the method of Goldfarb and Kondakova [8]. It was vacuum distilled, and converted into the picrate, from which it was regenerated and recrystallized from benzene; m.p. 85-86°.

5. 2-Amino-3-buta-1',3'-dienylpyridine was prepared by the method of Goldfarb and Kondakova [loc. cit.]. It was purified by steam distillation, and dried over calcium chloride; m.p. 74°.

6. 2-Amino-3-butylpyridine was prepared by hydrogenating 2-amino-3-buta-1',3'-dienylpyridine in presence of platinum catalyst, and was recrystallized from heptane; m.p. 46-47°.

7. 5-Bromo-2-aminonicotine was prepared according to Chichibabin and Kirsanov [6]. It was purified by vacuum distillation, followed by recrystallization from acetone; m.p. 138°.

8. 5-Bromo-2-amino-3-(4'-methylaminobut-1'-enyl)-pyridine (5-bromo-2-aminometan nicotine) was obtained by the action of acetic anhydride on 5-bromo-2-aminonicotine [9], and was purified by vacuum distillation followed by recrystallization from heptane; m.p. 103-104°.

9. 6-Bromo-2-methylaminomethyl-1,2-dihydro-1,8-naphthiridine was prepared by the action of alcoholic alkali on 5-bromo-2-amino-3-(3'-bromo-4'-methylaminobut-1'-enyl)-pyridine [loc. cit.], and was recrystallized successively from ether and heptane; m.p. 155-156°.

10. 6-Bromo-2-methyl-1,8-naphthiridine was obtained by a Hoffmann degradation of the methiodide of 6-bromo-2-dimethylaminomethyl-1,2-dihydro-1,8-naphthiridine [loc. cit.], and was purified by recrystallization from aqueous ethanol and then from benzene. It changes into an opaque yellow mass at 213-215°, and melts at about 350°.

11. 5-Bromo-2-amino-3-(1'-methyl-2'-pyrrolinyl)-pyridine was prepared by the action of alcoholic alkali on 5-bromo-2-amino-3-(3'-bromo-4'-methylaminobut-1'-enyl)-pyridine [loc. cit.], and was purified by recrystallization from ethanol; m.p. 127-129°.

12. 5-Bromo-2-hydroxy-3-(1'-methyl-2'-pyrrolinyl)-pyridine was prepared by the action of nitrous acid on 5-bromo-2-amino-3-(1'-methyl-2'-pyrrolinyl)-pyridine [loc. cit.], and was recrystallized from benzene; m.p. 163° (decomposition).

The spectra were photographed with the aid of a Hilgers spectrograph, medium size model, dispersion in the region of 360 mμ 44mμ/mm, and of 250 mμ 12 mμ/mm. The source of light was an arc between tungsten electrodes. The plates were 13 x 18 cm, iso-ortho, sensitivity 400, developer metol-quinol, acid fixing bath. The spectra were measured by the method of equal blackening, and the beam of light was split by a Huefner quartz rhombus. The intensity of the standard beam of light was varied by means of a rotating sector. Places of equal blackening were found visually. The scale of wave lengths was calibrated by means of a copper arc. Each spectrum was repeated a number of times, and a result was taken to be satisfactory if a point on the last section of a spectrum lay on the curve given by the preceding section. The concentration of the solutions was varied by factors of 10 and 100.

We have pleasure in expressing our profound gratitude to E. V. Shpolsky for allowing us to execute the optical part of this research in the Optical Laboratory of which he is the head, and for his interest and assistance.

SUMMARY

1. A comparison of the ultra-violet absorption spectra of a series of substituted 2-aminopyridines, in which substituents of differing degrees of unsaturation are situated in position 3 of the ring, shows that the absorption maximum is shifted when the side-chain double bonds are in conjugation with those of the pyridine ring.

2. The results of the absorption spectra studies confirm the proposed structure of the compound obtained by the action of acetic anhydride on 5-bromo-2-aminonicotine.

3. Comparison of the absorption curves of the base of m.p. 127-129° obtained by the action of alkali on 5-bromo-2-amino-3-(3'-bromo-4'-methylaminobut-1'-enyl)-pyridine and of other systems allows the conclusion to be drawn that this base, m.p. 127-129°, is a derivative of dihydronicotine.

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Institute of Organic Chemistry
Academy of Sciences USSR
V. I. Lenin Pedagogic Institute

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CHEMICAL TRANSFORMATIONS OF CELLULOSE MACROMOLECULES CAUSED BY OXIDANTS

PART 7. CHEMICAL TRANSFORMATIONS OF CELLULOSE DUE TO ITS OXIDATION WITH SODIUM HYPOCHLORITE

E. D. Kaverzneva, V. I. Ivanov, and A. S. Salova

Calcium hypochlorite and chlorine are the most widely used oxidants for the bleaching of cellulose materials. The careful use of these oxidants, under the appropriate conditions, makes the fibers whiter, without significantly affecting their strength and chemical stability, but deviation from these conditions readily leads to severe damage of the fibers. On the other hand, a number of industrial processes require a definite lowering of the viscosity of cellulose solutions, or modification of its physical and chemical properties (production of viscose, lacquers, oxycelluloses). It is not therefore surprising that numerous researches have been undertaken with the object of elucidating the changes produced in the properties of cellulose fibers by chlorine and hypochlorite. The general conclusion which emerged from these researches was that chlorine and the hypochlorite ion belong to the category of non-specific oxidants, which react with various parts of the cellulose macromolecule to produce, according to the reaction of the solution, either the "reducing" type of oxycellulose or the "acid" type [1].

All chemical studies of oxycelluloses were of a largely descriptive nature until well into the forties of this century. However, the past ten years have seen the elaboration of precise methods for the determination of the various functional groups of oxycelluloses, even when present in only minute amount in the macromolecule. Thus the analytical techniques applied and developed in our laboratories allow of the determination of total and "uronic" carboxylic groups with an accuracy of up to 0.05% of the weight of the sample, of aldehyde groups with an accuracy of up to 0.02%, and of carbonyl groups with an accuracy of up to 0.1%. These analytical advances make it possible to undertake a more profound study of the chemical processes taking place during the oxidation of cellulose by non-specific oxidants.

The chemical changes produced by such oxidants as chlorine, hypochlorite ion, perhydrol, atmospheric oxygen in alkaline media, and ultra-violet irradiation, and also the effect of pH changes on these processes, have not yet received any detailed study. Moreover, there are many mistaken beliefs current in this field. Thus Jurisch [2] says that perhydrol acts only on hydrate-cellulose, and only at concentrations of alkali greater than 8%. It appears from our work that chemical changes are observed in cellulose after the action of perhydrol at all pH values. The view has gained acceptance, on the basis of the work of Unruh and Kenyon [3], that nitrogen peroxide is a strictly specific oxidant of primary hydroxy groups, whereas we have found [4] that the activity of this oxidant is not so selective.

The object of the present research is to study the chemical processes taking place when hypochlorite, the most widely used oxidant, acts on cellulose. A peculiarity of hypochlorite is that the oxidant varies according to the pH of the medium; free chlorine predominates in acid solutions, and the concentration of undissociated hypochlorous acid rises as the reaction approaches neutrality, while with further rise in pH the concentration of hypochlorite ion rises [5]. The stability of HOCl is at a minimum at pH 6.7, and the maximum at pH 13 (Fig. 1).

Oxidation of monosaccharides by chlorine in acid solutions involves oxidation of the aldehyde group, as well as primary and secondary hydroxy groups, with subsequent fission of the carbon chain [6]. The primary hydroxyl of polyhydric alcohols appears to be the first to be oxidized [7].

The mechanism of oxidation of carbohydrates by halogens must be regarded as being far from being elucidated, although the work of Shilov and Yasnikov [8] is a valuable contribution thereto.

The present paper describes the results obtained for oxidation of purified cotton cellulose (0.05 N NaClO; 18-22°; modulus 1:20), at different pH of the solutions, uptake of oxygen being the same in all experiments.

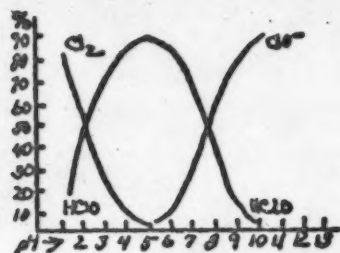


Fig. 1. Changes in the relations $\text{Cl}_2 \rightleftharpoons \text{HClO} \rightleftharpoons \text{HClO}_2$ at different pH values of the solution.

with warm 1% NaHCO_3 solution and with water. Analysis gave the following: ash content 0.19%; total COOH groups 0.07%, uronic acid COOH 0.07%; CHO 0.072%; iodine number 0.49; N 0.02%; viscosity of 0.2% solution 840 millipoise.

Oxidation. The NaClO solutions were prepared by saturation of cold 10% NaOH with chlorine. The NaOH concentration of a sample of the solution was determined separately, after decomposing hypochlorite with H_2O_2 , and the rest of the solution was made neutral by adding the calculated amount of hydrochloric acid. An equal volume of buffer solution was added to this basic solution, for the oxidation experiments, which were conducted with 0.049 N-NaClO at pH 4.6, 6.8, and 11. The modulus was 1:20 at 16-25°; the time needed for consumption of the scheduled amount of oxygen was derived from the difference between the active chlorine content of the experimental and of control solutions, at various times. The oxidized samples were then washed with a weak solution of NaHSO_3 and with water, demineralized in 0.5% acetic acid, and repeatedly washed with water. They were then allowed to dry, and were further dried at 50° before being analyzed.

Determination of total COOH-group content, from the reaction $\text{COOH} + \text{CH}_3\text{COOCa} = \text{RCOOCa} + \text{CH}_3\text{COOH}$ [9]. Portions (0.2-1.0 g) of oxycellulose were allowed to react for 24 hrs at room temperature with 0.5 N calcium acetate, prepared with CO_2 -free distilled water, and of pH 7.2-7.5. The free acetic acid formed was titrated with 0.02 N NaOH, to pH 8.3 (phenolphthalein indicator). The difference between the result of this titration and of a blank titration gave the carboxy group content. **Determination of uronic COOH-groups from the reaction $\text{CHO}(\text{CHOH})_4\text{COOH} + \text{HCl} \rightarrow \text{C}_5\text{H}_4\text{O}_2 + 3\text{H}_2\text{O} + \text{CO}_2$.** This was performed as a micro-variant of the decarboxylation method, using 12% HCl [10]; CO_2 was absorbed in 0.02 N-Ba(OH) $_2$, excess of which was titrated with 0.02 N-HCl.

Determination of aldehyde groups, from the reaction $\text{RCHO} + \text{NaOI} = \text{RCOOH} + \text{NaI}$ [11]. A portion of oxycellulose (0.2-0.5 g) was treated with 20 ml of ~0.03 N iodine solution + 10 ml of 0.05 M- $\text{Na}_2\text{B}_4\text{O}_7$ (pH 9.2) for 2 hrs at 25°, after which 30 ml of 0.1 N-HCl was added, and the solution was titrated with 0.01 N- $\text{Na}_2\text{S}_2\text{O}_3$; a control titration was done at the same time.

Determination of total carbonyl groups from the reaction $\text{RCOR} + \text{NH}_2\text{OH} \cdot \text{HCl} = \text{RR}'\text{CNOH} + \text{H}_2\text{O} + \text{HCl}$ [12]. After carboxyl groups had been neutralized with calcium acetate the cotton was washed with water, and dried, and a 1.0 g sample was treated with a freshly prepared 2.5% NH_2OH solution [200 ml of solution contain 5 g of $\text{NH}_2\text{OH} \cdot \text{HCl}$ and 20 ml of 0.5N-NaOH (pH ~5)]; for 2 hrs at room temperature. The solution is titrated with 0.1 N HCl, with bromophenol blue indicator, taking the color change from blue to yellowish-green as the end-point (pH 3.2); a blank titration is performed at the same time. The method was checked by determining total nitrogen in the preparations after condensation with NH_2OH . These analyses regularly gave a smaller amount of nitrogen than would correspond with that found by titration of the amount of CO-groups; the reason for this discrepancy was not discovered. The Tables give the content of total carbonyl groups (and of keto-groups, as the difference from aldehyde groups), in accordance with the determinations of nitrogen.

Viscosity was determined in 0.2% solutions of oxycellulose in cuprammonium reagent (NH_3 20%, Cu 1.5%), and in some cases for acetone solutions of nitrate esters. Additional oxidation of aldehyde groups

Oxidation was limited to use of 5-15 atoms of oxygen per 100 glucose residues, since when more oxygen is used the process is complicated by superimposition of secondary processes. Only for the study of certain special problems was more profound oxidation applied, using up to 200 atoms of oxygen per 100 glucose residues, in acid and alkaline solutions. In addition to this, all analyses were repeated for a number of preparations after additional oxidation of aldehyde groups with sodium hypodite in alkaline solution (pH 9.2).

EXPERIMENTAL

Pre-treatment of cotton. The cotton was treated with 1% NaOH for 10 hrs at 100°, washed, dried, and extracted with dichloroethane and 1:1 methanol-ether mixture. Before taking it for the oxidation experiments the cotton was again washed

with NaOI was performed under the same conditions as for their determination, but allowing more time. The results are given in Table 1.

The following conclusions emerge from these analytical data:

1. The following changes take place in the initial stages of oxidation of the macromolecule of oxycellulose by sodium hypochlorite in weakly acid solution (pH 4.6):

- (a) gradual rise in the COOH-group content;
- (b) gradual rise in aldehyde group content;
- (c) appearance of keto-groups;
- (d) the number of uronic acid carboxylic groups exceeds that of total COOH-groups.

2. The chemical changes due to oxidation in neutral solution (pH 6.8) are of the same order as in acid solutions, but the process proceeds much more rapidly than in the latter. The number of uronic acid carboxylic groups is greater than that of free COOH-groups.

3. The following is observed during oxidation in alkaline solutions (pH 11):

- (a) a more abrupt rise in total COOH-group content, in relation to bound oxygen, than in acid solutions;
- (b) almost complete absence of aldehyde groups (except in the case of deep oxidation);
- (c) formation of ketonic groups;
- (d) the number of uronic carboxylic groups is much smaller than the total number of COOH-groups.

These conclusions are shown graphically by the curves of Figs. 2 and 3.

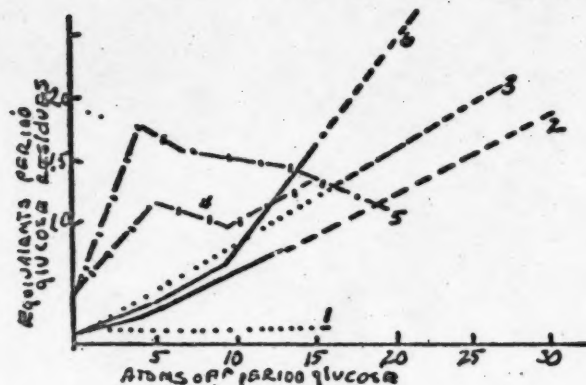
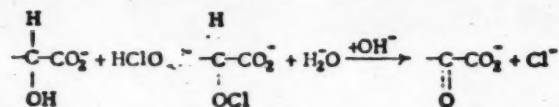


Fig. 2. Increase in functional group contents in oxycellulose as oxidation proceeds; 1) CHO, pH 11.0; 2) COOH, pH 4.6; 3) CHO, pH 4.6; 4) CO, pH 11.0; 5) CO, pH 4.6; 6) COOH, pH 11.0.

During equal intervals of time the curve representing binding of oxygen by cellulose lies much higher for neutral solutions than for acid or alkaline ones; this effect was taken to signify that the chief oxidant in the system Cl_2 , HClO , ClO^- is undissociated hypochlorous acid [13].

Yasnikov and Shilov [8] advance a different view, according to which HClO first gives an ester with a hydroxy group, and this ester then eliminates HCl , giving a carbonyl group:



This mechanism cannot be regarded as being proven, although there do exist arguments in its favor.

Position of the carboxylic groups in the glucose residues of the cellulose macromolecules

It follows from a study of Table 1 that with oxidation in acid or neutral solutions the number of "uronic" COOH-groups exceeds that of free carboxylic groups. We have explained this [14,15] as being due to presence of traces of carbonate esters, and to formation of lactones from part of the uronic COOH-groups of these oxycelluloses. Since we have as yet no accurate way of estimating the extent of such lactone formation, the determination of non-uronic COOH-groups in these products is difficult.

Oxidation of the primary OH-group at C_6 to COOH is evident in the products of alkaline oxidation, as well as accumulation of non-uronic COOH-groups. It may be supposed that some of these will be at the end of chains, but it follows from calculation of the number of non-uronic COOH-groups per macromolecule of oxycellulose

TABLE 1

Analysis of oxycelluloses. (All values for functional groups are given as equivalents per 100 glucose residues).

No. of preparations	Conditions of oxidation	pH of reaction solution	No. of atoms of O bound (from amount of NaOCl used)	Yield of oxycellulose, %	Degree of polymerization	COOH-groups			Carbonyl groups	Aldehyde groups	Carbonyl groups (total), from cellulose oxime nitrogen	"Keto" groups
						total (by the Ca acetate method)	"uro-nic"	non-uronic (by difference)				
4	0.049 N NaOCl, 19-22°, 7 hrs (acetate buffer) 1:20	4.6	4.25	~100	500	0.28	0.26	Nil	—	0.32	2.14	1.82
1	" 57 hrs	4.6	7.09	~97.2	390	0.425	0.76	?	—	0.58	2.20	1.52
7	" 14 days	4.6	13.16	95.7	220	0.74	1.04	?	0.22	1.02	2.47	1.45
Prep. b-2	0.13 N NaOCl, 24 hrs., 17°	5	20.2	92	—	0.57	1.10	?	—	0.98	1.96	0.98
1-deep	0.23 N NaOCl, 25°, 24 hrs	3.1	44.6	~84	114 (nitrate)	1.66	1.91	?	0.17	1.68	2.17	0.49
2-deep	0.2 N NaOCl, 22° 24 hrs (without drying)	~1	—	~48	—	2.95	3.82	?	—	2.14	3.71	1.57
5	0.049 N NaOCl, 22-25°, 2 hrs (phosphate buffer)	6.86	4.96	100	475	0.25	0.33	?	—	0.32	1.55	1.23
8	" 19-20°, 5 days	6.86	7.59	96.6	245	0.61	0.83	?	—	0.49	1.73	1.24
2	" 22-28°, 7.5 hrs.	6.86	9.11	96.8	342	0.76	1.01	?	0.09	0.53	1.63	1.10
6	0.049 N NaOCl, 20°, 6 hrs (carbonate buffer)	11	4.96	100	420	0.38	0.43	?	—	0.16	1.26	1.10
3	" 56.5 hrs, 20°	"	9.11	98.6	390	0.65	0.57	0.08	0.0	0.16	1.09	0.93
9	" 19-20°, 20 days	11	14.38	95.9	180	1.47	0.71	0.76	0.0	0.17	1.50	1.33
TsB-3*	Ca(OCl) ₂ , 20°, 4 hrs in 2 stages	9.5	Given	85	64	3.49	1.58	1.91	—	1.73	3.81	2.08
TsB-1*	"	9.5	Given	75	32	4.32	3.06	1.26	—	1.33	5.11	3.78
Prep. B	0.094 N NaOCl, 1:20, 24°, 3 days (borate buffer)	9	—	98.4	—	1.44	0.83	0.61	—	0.20	1.57	1.37
	Initial cellulose					0.15	0.25	?	0.025	0.20	0.51	0.31

* We obtained the preparations TsB-1 and TsB-3 from F. P. Komarov of TsNIB, for which we thank him.

that it must be greater than one. It follows that formation of some of the COOH-groups is associated with opening of the pyranose rings of the glucose residues.

Carbonic acid esters are present in the products of oxidation in acid and neutral solutions, but their number is small, and does not rise as depth of oxidation increases. They are apparently decomposed as formed, with breakdown of the cellulose chain.

Position of aldehyde groups in the glucose residues of the cellulose chain

In order to ascertain the position of the aldehydic groups in the glucose residues they were oxidized to carboxylic groups under specific conditions, with the object of finding whether uronic or non-uronic acids are

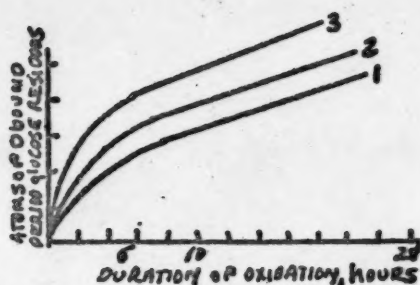


Fig. 3. Oxygen used for oxidation of cellulose at various pH: 1) pH 11.0; 2) pH 4.6; 3) pH 6.8

group content of the residue, making it impossible to draw up a balance of functional groups. This effect is particularly evident for highly oxidized preparations in acid solution (Nos. 7-9). It appears from a consideration of the data for low degrees of oxidation (experiments Nos. 1, 2, 3, and 4), and for deep oxidation in alkaline solution (Nos. 5 and 6), that the content of uronic carboxylic groups rises after oxidation of aldehydic groups, suggesting that some of these groups must be at position 6 of the glucose residues.

A conclusion of this sort could not be made for the products of deep oxidation of cellulose in acid solution, since the number of uronic carboxylic acid groups falls abruptly, owing to the solubility of these products. At first sight it is hard to understand the reason for the rise in the number of ketonic groups after oxidation of aldehydic groups, which appears to be a regular feature of products of deep oxidation (Nos. 5-9). We have suspected that during oxidation with sodium hypodite in weakly alkaline solution hydroxyketone groupings can undergo oxidation, in addition to aldehydic groups, after conversion into endiol groupings.



This reaction could lead to increase in the number of ketonic groups without formation of new carboxylic groups.

However, as was shown in our previous publication [15], the hydroxy-ketone grouping of oxycelluloses does not undergo conversion into endiol at pH < 10, and is not oxidized by hypiodite. For this reason a different explanation of the apparent rise in ketonic groups must be sought, and this may be found in formation of lactones of newly formed carboxylic groups; the lactone reacts with hydroxylamine instead of the oxidized aldehyde group. This gives the appearance of a rise in ketonic group content. The nitrogen content of the cellulose oximes obtained before and after oxidation of aldehydic groups was about the same, in accordance with this supposition; aldoxime nitrogen is replaced by an equivalent amount of hydroxamic acid nitrogen.

The basic conclusion to be drawn from these experiments is that some of the aldehyde groups of the oxycelluloses obtained by both acid and alkaline oxidation are at position 6 of the glucose residue. The number of aldehydic groups in this position is much smaller after alkaline than after acid oxidation. The number of other aldehyde groups greatly exceeds one per oxycellulose macromolecule.

Attempt at formulating a scheme of oxidation processes associated with the action of sodium hypochlorite on cellulose

Our experiments have led us to the conclusion that oxidation of cellulose with sodium hypochlorite involves formation not only of carboxylic and aldehydic groups, as has been shown by numerous authors, but also of α -hydroxyketone groupings, carbonate groupings, and lactone bonds. The velocity of simultaneously proceeding oxidation processes depends on the pH of the solution, and they lead to production of oxycelluloses of differing chemical properties.

produced. The products of selective oxidation of aldehydic groups with NaOI at pH 9.2 were washed and demineralized, and were analyzed for all their functional groups. This treatment should in theory lead to increase in the content of total free carboxylic groups, by an amount equivalent to diminution in the content of aldehydic groups. Should these aldehyde groups have been located at carbon atom 6 of the glucose residues the content of uronic carboxylic groups should also rise. The results of these experiments are given in Table 2.

It is, however, difficult to draw firm conclusions from these experiments, since during oxidation in alkaline solutions considerable dissolution of the oxycelluloses produced takes place, the more oxidized units of the chains having a stronger tendency to pass into solution. This leads to a lowering of the carboxylic

TABLE 2

Analyses of oxycelluloses before and after additional oxidation of aldehydic groups (as equivalents per 100 glucose residues)

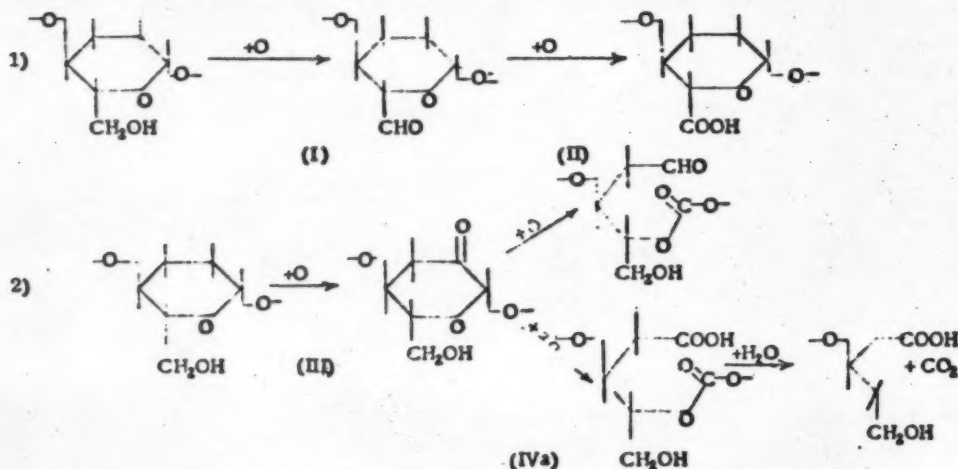
Expt. No.	pH during oxidation with NaOCl	Additional oxidation with	COOH-groups (uronic)		CO + COH by titration of liberated HCl		CHO		CO (by difference)		CHO at C ₆	Total oxime N	
			before	after	before	after	before	after	before	after		before	after
1	4.6	NaIO at pH 9.2	1.04	1.51	2.98	1.91	0.38	Nil	2.0	1.91	0.47		1.56
2	4.6	ditto	1.04	1.39	3.01	1.97	1.0	"	2.02	1.97	0.35		
3	5	"	1.10	1.32	3.01	1.85	0.98	"	2.03	1.85	0.22	1.33	1.28
4	9.0	"	0.83	0.83	2.49	2.43	0.20	0.035	2.79	2.39	0		1.53
5	9.5	"	3.08	3.38	5.39	5.95	1.33	—	4.05	5.95	0.32	6.02	5.61
6	9.5	"	1.58	1.91	4.34	4.74	1.73	—	2.61	4.74	0.32	3.99	—
7	3.1	ClO ₂ in acid solution	1.91	1.13	2.38	3.7	1.21	0.05	1.20	3.64			
8	3.1	NaIO at pH 9.2	1.91	1.18	2.38	3.65	1.39	Nil	0.99	3.65		2.08	1.71
9	1	ditto	3.74	1.69	6.20	5.97	2.14	—	4.06	5.97		3.59	

Two parallel reactions proceed simultaneously in acid solutions:

(1) oxidation of primary OH-groups at C₆ to give aldehydes, which are further oxidized to carboxylic groups;

(2) formation of α -hydroxyketones, which are further oxidized with opening of the ring, and formation of carbonic acid esters.

Oxidation in acid solutions; pH 3-5:



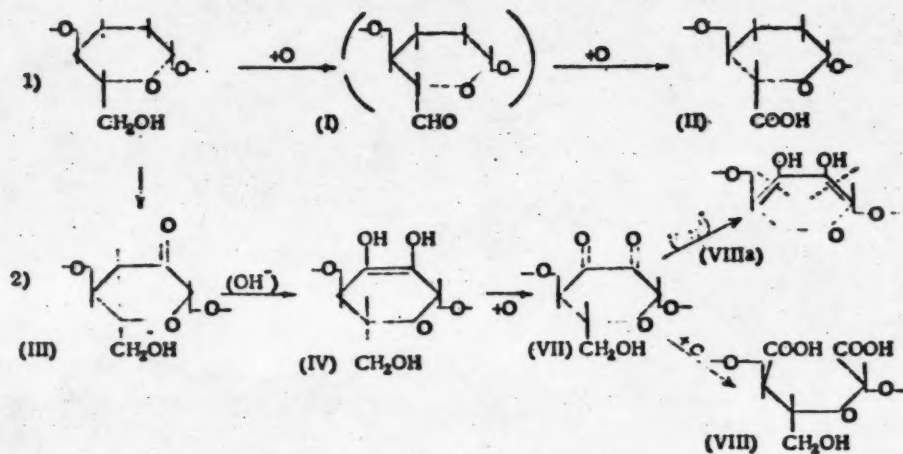
The oxycellulose formed has reducing properties (C₁ and C₆ aldehyde groups, α -hydroxyketone groups), and is readily depolymerized in alkaline solution, owing to hydrolysis of carbonic acid ester residues in the chain, and to enolization of aldehydic and ketonic groups [16]. Additional oxidation of aldehydic groups leads to

Increase in the number of uronic carboxyls, at the expense of those aldehydic groups which are at position 6. Not all the carboxylic groups are free ones, some of them being included in lactone rings, as a result of which direct determination of acidity does not reveal all of them.

Oxidation processes in neutral solution are analogous to those in acid solution. In alkaline solutions the same two reactions (formation of aldehydes and ketones) initiate the process, which then develops differently. Stage I proceeds very quickly, and C₆ aldehydic groups do not accumulate, but are rapidly further oxidized to uronic carboxylic groups (II).

In the second reaction the monoketone (III) formed isomerizes to the endiol (VI), which is rapidly oxidized to the diketone (VII), followed by opening of the ring, with formation of two carboxylic groups, giving a compound with a shorter carbon chain (VIII).

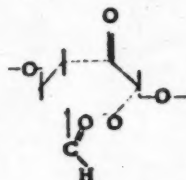
Oxidation in alkaline solution; pH 11.



There are no carbonic acid esters, and only a very few aldehydic groups, in oxycellulose obtained in alkaline solution. The esters, if formed, undergo hydrolysis in alkaline solution, and aldehydes are rapidly oxidized to carboxylic groups. On the other hand, there is a high content of non-uronic carboxylic groups formed by opening of the pyranose ring at points of inclusion of keto- and diketone-groups.

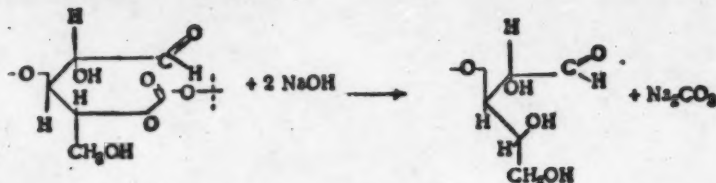
There are initially no lactone groups present in oxycellulose formed in alkaline solution, but these groups are formed during acid treatment of the products for their demineralization.

The reaction mechanisms given include only the simpler, partly experimentally confirmed, transformations of glucose residues of the cellulose macromolecule. There can be no doubt that oxidation of primary OH-groups at C₆ and of secondary groups at C₂ (or C₃) may take place in the same glucose unit.



In such cases a large number of different decomposition products should be formed, and an indication that the reaction may proceed in this way is afforded by the fact that our experiments on condensation with NH₂OH gave only negligible amounts of glucosamine, with larger amounts of some as yet unidentified nitrogen-containing products [15].

The fall in the degree of polymerization found in acid oxidation media is not connected with presence of aldehydic groups, as is shown by the stability under these conditions of dialdehyde-cellulose. Hydrolytic decomposition in acid solutions is accelerated owing to hydrolysis of carbonic acid esters, the amount of which does not rise with progressive increase in depth of oxidation. This indicates that they are decomposed as they are formed.



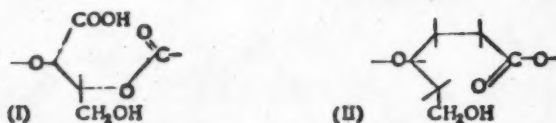
Apart from this, the stability of glucoside bonds in acid solutions is lowered when carboxylic groups are formed [17,3].

Breaking of chains during oxidation in alkaline solutions takes place under the influence of aldehydic groups which have become modified to the enolic form; the stability of the glucoside bond is lowered by proximity to a double bond [18]. It appears from the more recent experimental data on the stability of glucosides in alkaline solutions that keto-groups situated at the α - or β -position relative to the glucoside bond also greatly reduce the stability of the latter [19].

The reaction mechanism proposed by us explains many of the properties of oxycelluloses, such as rapid increase in COOH-group content during oxidation in alkaline solution, chiefly due to formation of non-uronic carboxylic groups, as a result of fission at keto-carbons. Our scheme is also in conformity with those structural features which cause excess evolution of CO_2 during determination of uronic acids (esters of carbonic acid, lactones). It logically explains the abrupt fall in viscosity observed when oxycelluloses from acid oxidation are placed in alkaline solution (decomposition of carbonic acid esters, enolization). The impossibility of accumulating ketonic groups in the cellulose chain, owing to their further oxidation as they are formed, is also understandable in the light of our reaction scheme.

Our scheme also explains how it is that HIO_4 in acid solution gives high-molecular "dialdehyde-celluloses" with a high aldehydic group content, or that dry N_2O_4 gives high-molecular carboxyl-celluloses, while treatment with hypochlorite does not give highly oxidized high-molecular oxycelluloses. Hypochlorite-type oxidation is associated with formation of functional groups, some of which cause degradation of the chain in acid and neutral solutions, and others give this effect in alkaline solution. It is thus not possible to provide conditions such that the oxycellulose chain would be stable, and to this is due the non-specificity of hypochlorite as an oxidant.

Staudinger and Sohn [20], who in 1939-1940 proposed a scheme for the oxidative degradation of cellulose, attributed the instability of the products to the action of alkalis to formation in the chain of modified glucose residues of the type of carbonic acid ethers (I) and esters (II).



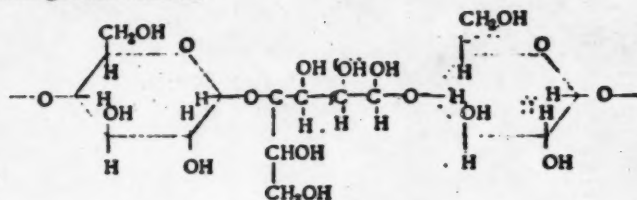
Both schemes were purely speculative, and were not backed by any experimental evidence whatsoever.

Schulz [21] in 1947 tried to provide an experimental basis for Staudinger's scheme, consisting of reaction velocity measurements. Finally, Heuser suggests in his monograph [22] a variant of Staudinger's scheme, also without any experimental basis. Nor does the very recently published paper of Haskins and Hogsed [23] make any real contribution; they suggest a variant of the mechanism already considered by us, depending on weakening of the glucoside bond by enolization of aldehydic groups [18]. We thus see that up to now no reaction schemes having any experimental basis whatsoever have been advanced for the oxidation of cellulose by non-specific oxidants.

Our paper represents the first attempt at providing such a scheme, based on chemical evidence. Some of the assumptions made earlier have been confirmed by our findings; in particular, the presence of carbonic

acid ethers (esters) has been demonstrated with certainty in celluloses oxidized in acid solution, although in very small amount. We have also demonstrated the presence of the hydroxyketonic grouping. Presence of diketones is very probable, although we have no direct evidence for this. Finally, our results have shown the presence in oxycelluloses of ester groups other than carbonate ones; the ease of their formation in acid solution and of their hydrolysis in alkaline solution incline us to believe that we here have to do with lactone formation in separate glucose units, similarly to lactone formation in low molecular weight hydroxy-acids.

We were not able to establish presence of ester type bonds, as proposed by Staudinger and Heuser, since the reaction of formation of hydroxamic acids tells us nothing of the location of the ether groups. Our observation that such groups are formed secondarily when oxycelluloses are treated with aqueous acids cannot be made compatible with Staudinger's ester theory. The formation chiefly of uronic carboxylic groups in the initial stages of oxidation is an additional argument against oxidation of carbon atom 1, since this should lead to formation of non-uronic COOH-groups. The possibility of oxidation at C₁ cannot, however, be entirely excluded, especially if we take into account Streptikhoev's views [24] as to the possible presence in the cellulose chain of non-cyclic glucose residues.



There are many other details of the oxidative process for which we are not at the moment able to give unambiguous explanations. We regard the mechanism advanced by us as being only a first approximation in accordance with the experimental material obtained by us for reactions of oxidation of cellulose.

SUMMARY

1. Chemical changes in the structure of cotton cellulose due to oxidation with sodium hypochlorite at different pH have been investigated by means of specific quantitative micromethods.
2. The following groups have been found in the oxycelluloses obtained by hypochlorite oxidation: uronic and non-uronic carboxylic groups, C₆ aldehydic groups, α -hydroxyketonic and lactone groups, and carbonic acid ester (ether) groupings.
3. The oxycelluloses obtained by oxidation in acid and neutral solution have a similar structure, different from that obtained in alkaline solution.
4. A reaction mechanism is advanced for the oxidative degradation of cellulose by the action of sodium hypochlorite at various pH. This mechanism satisfactorily explains the chemical behavior of the oxidation products.
5. The various oxidative processes shown to occur may be utilized for the better control of such processes, and for the preparation of cellulose oxidation products of known properties.

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Institute of Organic Chemistry
Academy of Sciences USSR

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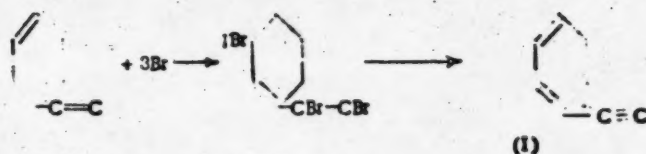
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1-ETHINYLCYCLOHEXA-1,3-DIENE AND ITS DERIVATIVES

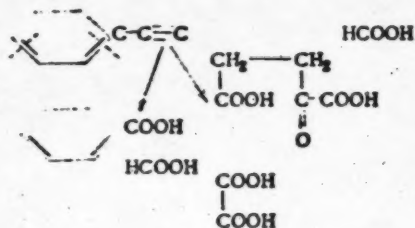
A. D. Petrov and A. V. Kulikova

We took as the starting material for the synthesis of this new-acetylenyl hydrocarbon 1-vinylcyclohex-3-ene, which is readily available. The acetylenic hydrocarbon could not be obtained by successive chlorination and dechlorination of the vinyl hydrocarbon, but bromination at -2° to $+2^\circ$, giving the tribromide, followed by debromination gave the required product. The record of bromination of vinylcyclohexene by Lebedev [1], and the results of our study of the product obtained allow us to assume that the reaction proceeds as follows:

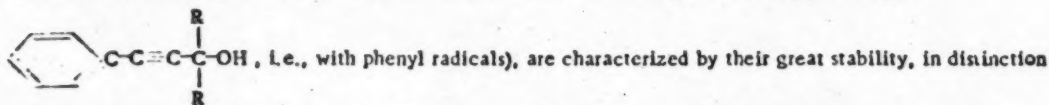


A molecule of bromine first adds on the double bond of the side-chain, and an atom of bromine enters the ring according to the mechanism of Tishchenko [2], with displacement of the double bond to the α -position. We at first oxidized hydrocarbon (I) under the conditions recommended by Lebedev [3] for oxidation of vinylcyclohexene, but we obtained only benzoic acid.

It is evident that 1-ethinylcyclohexa-1,3-diene, being a derivative of dihydrobenzene, does not undergo fission at the double bonds when treated with chromic acid mixture, but undergoes further dehydrogenation of the ring. We next tried oxidation with 0.5% potassium permanganate, whereby we obtained cyclohexa-1,3-diene-1-carboxylic acid and ketoglutaric acid, suggesting that oxidation proceeds as follows:



The presence of a triple bond in hydrocarbon (I) was confirmed by its hydration, which gave 1-acetylcyclohexa-1,3-diene, identified as its 2,4-dinitrophenylhydrazone, m.p. 230° [that the hydrocarbon (I) is not phenylacetylene is shown by the fact that the dinitrophenylhydrazone of acetophenone melts at 249°]. The hydrocarbon (I) gave the corresponding tertiary acetylenic alcohols, by a Grignard reaction with diisopropyl ketone or benzophenone. These alcohols, similarly to Malenok's tertiary alcohols [4] (of the type



to acetylenic alcohols with conjugated multiple bonds in aliphatic radicals. They do not polymerize when stored for eight months.

EXPERIMENTAL

Several kilograms of 1-vinylcyclohex-3-ene was obtained by heating divinyl in a steel autoclave for 6-8 hrs at $140-160^\circ/50$ atm. It had b.p. $49-51^\circ/50$ mm, d_4^{20} 0.8299; n_D^{20} 1.4647; found MR_D 35.96; calculated MR_D 36.03.

Bromination was conducted to the tribromide, the amount of bromine adding on being derived from the gain in weight of the flask with the product. The tribromide is a dark, slightly fuming liquid, with an acrid odor. It was debrominated by heating under reflux on a water bath with 20% alcoholic potassium hydroxide, which was added in small portions, each addition being followed by considerable evolution of heat. After completion of the reaction the potassium bromide formed was filtered off, the alcohol was distilled off from the filtrate, the residue was diluted with water, and the solution was extracted with ether. The extract was fractionally distilled, giving a fraction of b.p. 52-54°/49 mm, d_4^{20} 0.8489; n_D^{20} 1.4865; found M_R 35.15; calculated M_R 33.94, yield 20% of the 1-vinylcyclohex-3-ene taken.

Oxidation of the fraction of b.p. 52-54°/49 mm. 1 g of potassium permanganate was added to an emulsion of 4 g of the hydrocarbon in 200 ml of water; the reaction proceeded energetically, and the solution was rapidly decolorized, 24 g of permanganate being added altogether. The products included acids only, and after acidification crystals of 2,3-dihydrobenzoic acid (cyclohexa-1,3-diene-1-carboxylic acid), m.p. 93.5-94° [5]°. This acid has a tendency towards conversion into benzoic acid when boiled with water, during recrystallization. Its amide melts at 105°.

Found in amide of m.p. 105° % N 11.87

Calculated for C_7H_8ON % N 11.3

The filtrate from this acid was made neutral with aqueous ammonia, and the silver salt of α -ketoglutaric acid was precipitated from it.

Found %: C 15.93; H 1.64; Ag 59.5

$C_5H_4O_5Ag_2$. Calculated %: C 16.6; H 1.10; Ag 59.9

Hydration of the hydrocarbon (I) gave a ketone, the 2,4-dinitrophenylhydrazone of which melted at 230-231°:

Found % N 19.01

$C_{14}H_{14}N_4O_4$. Calculated %: N 18.65

Synthesis of 1-(cyclohex-1',3'-dienyl)-4-methyl-3-isopropylpent-1-yn-3-ol

1-Ethynylcyclohexa-1,3-diene (24 g) was added in small portions to a solution in 150 ml of ether of 3.7 g of Mg and 16.4 g of C_2H_5Br . The reaction proceeded energetically; with evolution of gas, and the mixture was then heated for 3 hrs, and left overnight. A solution of 18 g of diisopropyl ketone in ether was then added; the reaction, which commenced after half of the ketone had been added, proceeded violently, and required constant cooling. The complex was decomposed with ammonium chloride, and the product was fractionated, giving 9.2 g of a fraction of b.p. 162-164°, n_D^{20} 1.5030; d_4^{20} 0.8830; found M 223; calculated M 218.

Found %: C 82.32; H 10.36

$C_{15}H_{22}O$. Calculated %: C 82.50; H 10.01

Found %: OH 6.89 (Tserevitinov)

$C_{15}H_{22}O$. Calculated %: OH 7.8

The OH-group content was determined more accurately by the method of dehydration with iodine [6]; it amounted to 90% of theoretical.

Synthesis of 3,3-diphenyl-1-(cyclohexa-1',3'-dienyl)-prop-1-yn-3-ol

17.7 g of benzophenone, 10 g of 1-ethynylcyclohexa-1,3-diene, 10.5 g of C_2H_5Br , 2.3 g of Mg, and 100 ml of ether was allowed to react as above, giving 14 g of a fraction of b.p. 182-185°/26 mm; n_D^{20} 1.5810; d_4^{20} 1.0767; found M 290; calculated M 291.5.

Found %: C 87.86; H 6.04

$C_{21}H_{18}O$. Calculated %: C 88.10; H 6.30

Found %: OH 4.89 (Tserevitinov)

$C_{21}H_{18}O$. Calculated %: OH 5.85

* 2,3-Dihydrobenzoic acid melts at 94°, and its amide at 105°.

The OH content, determined by dehydration with iodine, was 96% of theoretical.

The presence of a triple bond in the alcohol was confirmed by its hydration; the 2,4-dinitrophenylhydrazone of the keto-alcohol so obtained melts at 182-183°.

Found %: N 11.76

$C_{17}H_{24}N_4O_6$. Calculated %: N 11.6

SUMMARY

1. 1-Ethynylcyclohexa-1,3-diene has been prepared, its physico-chemical properties have been studied, and its structure has been established from a study of its oxidation products.

2. Hydration of 1-ethynylcyclohexa-1,3-diene gives 1-acetylcyclohexa-1,3-diene, identified as its 2,4-dinitrophenylhydrazone, m.p. 230-230.5°.

3. The acetylenic alcohols 1-(cyclohex-1',3'-dienyl)-4-methyl-3-isopropylpent-1-yn-3-ol and 3,3-diphenyl-1-(cyclohex-1',3'-dienyl)-prop-1-yn-3-ol have been prepared by the Iotzich-Grignard reaction, and their physico-chemical properties have been studied.

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D. I. Mendeleev Chemico-Technological Institute

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